

THE STEREOCHEMISTRY OF ACENAPHTHYLENE

GLYCOLS.

by

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successfully sustained an oral examination on the
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Members of
Committee.

6 May, 1937.

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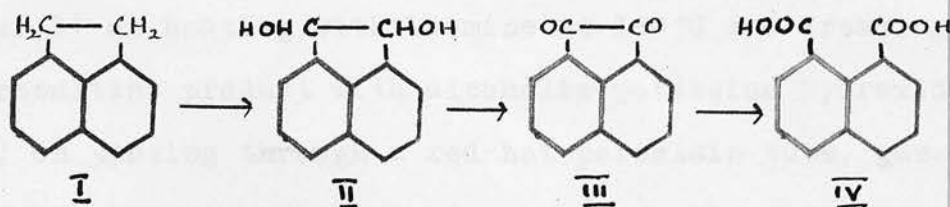
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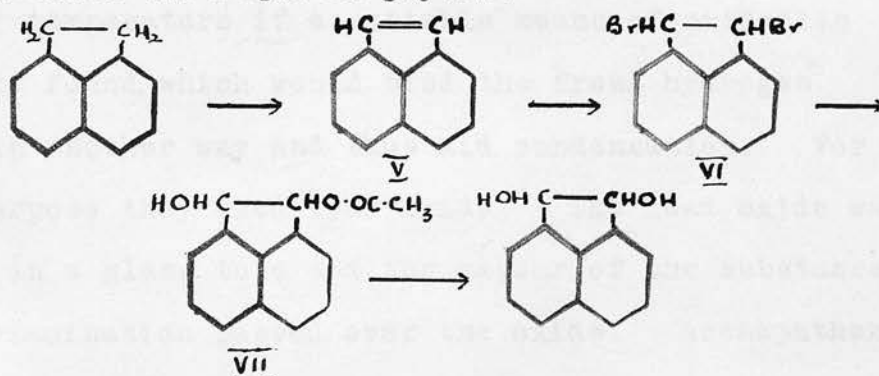
As a rule the number of optical isomers of a compound containing several asymmetric carbon atoms is 2^n , where n is the number of asymmetric carbon atoms of different configurations present in the compound. In the case where two or more similar asymmetric atoms occur in the same molecule some of these possibilities disappear. Thus compounds containing two asymmetric carbon atoms which are similar in structure, exist in three isomeric forms, instead of four, namely, the dextro- and laevo-rotatory forms and the meso-, or internally compensated type.

To this last class of compounds belongs acenaphthylene glycol, first prepared, in 1899, by Ewan and Cohen (J.C.S., 55, 578), who undertook a set of experiments aiming at the preparation of the intermediate

products of the oxidation of acenaphthene (I) to naphthalic acid (IV). They postulated the possibility of preparing the previously unknown acenaphthylene glycol (II) and also acenaphthene quinone (III).



The glycol was successfully prepared, in the following steps, from acenaphthene. Acenaphthylene, obtained by the controlled oxidation of acenaphthene, was converted to the dibromide (VI), from which the mono-acetate (VII) was prepared. Hydrolysis of this compound yielded the required glycol.

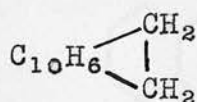


Discovery, Synthesis and Constitution of Acenaphthene and Acenaphthylene.

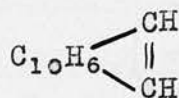
It is in Berthelot's memoir 'Des Carbures Pyrogénés,' published in 1867, (Annales de Chimie et de Physique, 4e series, t. XII) that the first mention of acenaphthene is made. This chemist discovered it amongst the products of the distillation of coal-tar,

and in 1872 Berthelot and Brady (Compt.rend., 1872, 74, 1463) succeeded in synthesising the hydrocarbon from ethyl naphthalene, which was prepared from bromonaphthalene, ethyl iodide and sodium. Ethyl naphthalene, either 1) on heating with bromine at 180°C and treating the resultant product with alcoholic potassium hydroxide, or 2) on passing through a red-hot porcelain tube, gave acenaphthene.

Acenaphthylene, containing an unsaturated bridge between the peri-positions, was first prepared by Behr and van Dorp (Ber., 1873, 6, 753), in their study of the pyrogenic reactions of hydrocarbons; they suggested that these changes might proceed more smoothly and at a lower temperature if a suitable means of oxidation could be found, which would bind the freed hydrogen atoms in another way and thus aid condensation. For this purpose they used lead oxide. The lead oxide was heated in a glass tube and the vapour of the substance under examination passed over the oxide. Acenaphthene (I) on such treatment was found to be converted into a new hydrocarbon by the loss of two hydrogen atoms; hence they named it acetylene-naphthalene (II), a name which was later changed to acenaphthylene.



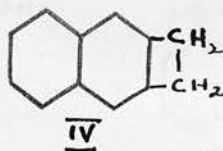
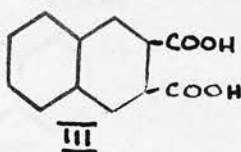
I



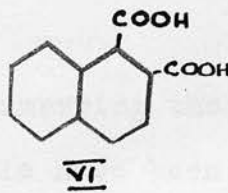
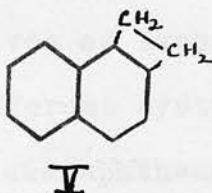
II

A further advance towards the establishment of the

constitution of these compounds was made when Behr and van Dorp (Ann., 1874, 172, 263) found that on oxidation acenaphthene and acenaphthylene yielded naphthalic acid. The C_2H_4 - bridge of acenaphthene and the C_2H_2 - bridge of acenaphthylene must, therefore, occupy the same positions in the naphthalene nucleus as do the carboxyl groups in naphthalic acid. At this time it was assumed that these carboxyl groups occupied the 2:3- positions and thus formulae III and IV were postulated for naphthalic acid and acenaphthene, respectively.



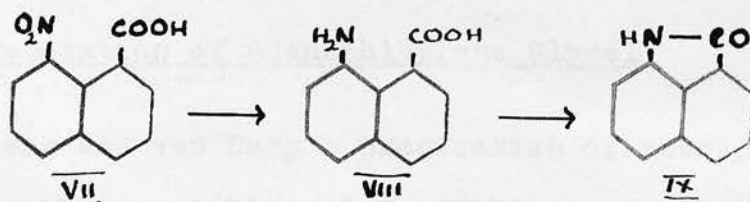
Terrisse (Ann., 1885, 227, 133) examined the naphthalic acid obtained by oxidation of acenaphthene and prepared from it naphthalic fluorescein and naphthalic eosin thus concluding that the carboxyl groups were ortho substituents. He also drew attention to the fact that, since Berthelot had synthesised acenaphthene from ethyl naphthalene, which is certainly a 1-substituted compound, neither acenaphthene, nor naphthalic acid, could be a 2:3- product, and suggested the amended formulae V and VI.



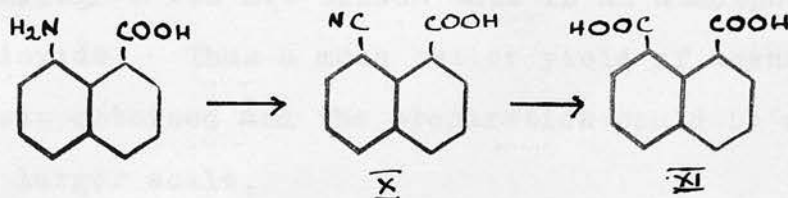
The work of Ekstrand (Ber., 1886, 19, 1131; J. pr. Chem., [2], 1888, 38, 241) conclusively showed that

1:8-naphthalene derivatives displayed properties hitherto observed only in ortho- derivatives and finally, in 1887, Bamberger and Philip (Ber., 20, 237) synthesised naphthalic acid and thus established our present views regarding the constitution of the compounds in question.

On nitration of 1-naphthoic acid Ekstrand (Ber., 1885, 18, 2881) obtained two isomeric mononitro-derivatives one of which (VII), on reduction to the corresponding amino-acid (VIII) readily formed naphthostyryl (IX), thus proving it to be a 1:8- compound.

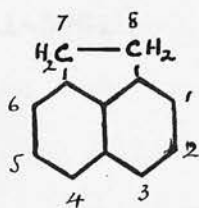
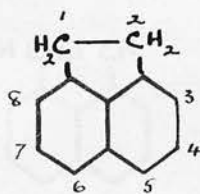
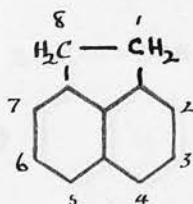
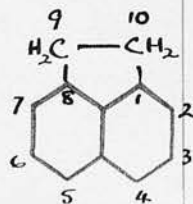


Philip and Bamberger (loc. cit.) diazotised the 8-amino-1-naphthoic acid and then carried out a Sandmeyer reaction, thus replacing -NH_2 by -CN (X), and on hydrolysis obtained naphthalic acid (XI).



This constituted the final proof that naphthalic acid, and hence acenaphthene and acenaphthylene, are 1:8- derivatives of naphthalene.

Four different systems of numbering the carbon atoms in the acenaphthene molecule have been suggested by various workers at different times.

IIIIIIIV

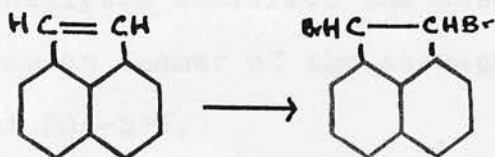
The systems III and IV have the obvious advantage over I and II that no change of numbering is necessary on passing from compounds of the naphthalene to those of the acenaphthylene series. In the present thesis system IV will be used.

Preparation of Acenaphthylene Glycol.

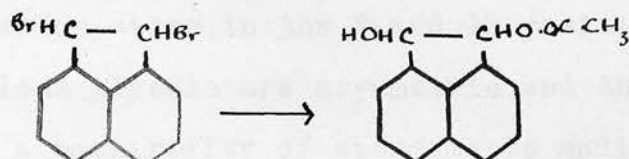
In Behr and van Dorp's preparation of acenaphthylene only small quantities of acenaphthene could be used for dehydrogenation and the method employed later by Dziewonski and Rapalski (Ber., 1912, 45, 2491) was much superior. By this method acenaphthene vapour was passed through a red-hot silica tube in an atmosphere of carbon dioxide. Thus a much better yield of acenaphthylene was obtained and the preparation could be carried out on a larger scale.

Acenaphthylene dibromide was prepared by Blumenthal, (Ber., 7, 1093), by bringing molecular proportions of bromine into contact with an ethereal solution of acenaphthylene. On evaporation of the excess of ether a reddish residue was obtained, which on recrystallisation, gave almost white needles of the dibromide, melting at

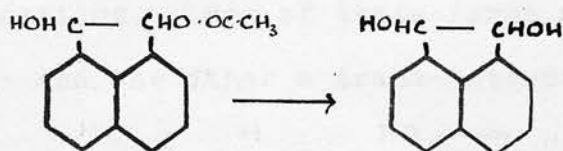
121-3°C.



Ewan and Cohen (*loc. cit.*) boiled acenaphthylene dibromide with potassium acetate and excess of glacial acetic acid and obtained, on neutralisation with sodium hydroxide, yellow needles of the monacetyl derivative, melting at 122-122.5°C.

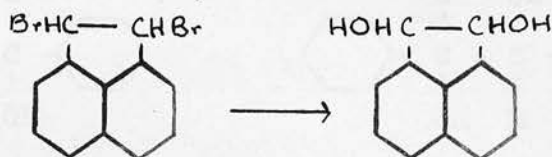


This compound was dissolved in methyl alcohol and boiled with potassium hydroxide, yielding, on cooling, long needles of the glycol, quoted as melting at 204-5°C.



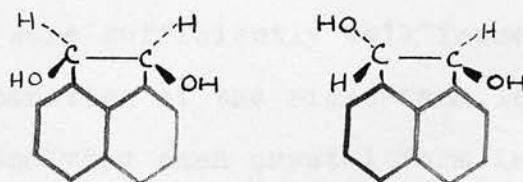
Graebe and Jequier, (*Ann.*, 290, 205), in 1896 gave a more convenient method of preparing acenaphthylene glycol, and obtained greatly increased yields, by boiling acenaphthylene dibromide with a large excess of water. On cooling the aqueous mixture, the glycol prepared by Ewan and Cohen (*loc. cit.*) crystallised out, but it was also found that, on evaporation of the mother liquors a smaller quantity of a substance, much more soluble in water and alcohol and melting about 145°C,

was obtained. Analysis confirmed the assumption that this substance was an isomer of the acenaphthylene glycol melting at 204-5°C.



Stereochemistry of cis- and trans-isomers.

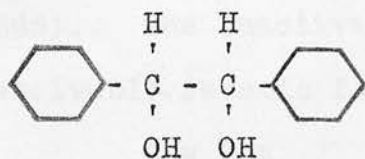
Graebe and Jequier (*loc. cit.*) also pointed out that the carbon atoms in the 9 and 10 positions of the acenaphthylene glycols are asymmetric and that there is, therefore, a possibility of stereomeric modifications occurring. Since the alcoholic solutions of the glycols displayed no rotatory power, they concluded that the two forms isolated must be the meso- and racemic modifications. One of these forms must, obviously, have a cis- and the other a trans- structure.



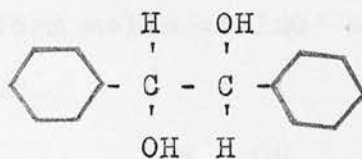
As is evident from the spatial diagrams, the cis-form has a plane of symmetry and must therefore be the internally compensated, meso-, form, whereas the trans-form, having no plane or centre of symmetry, must exist as dextro- and laevo-rotatory isomers and hence also as a racemate.

By analogy with the hydrobenzoin, it was to be expected that the lower melting acenaphthylene glycol

would prove to be the resolvable form and the higher melting glycol the inactive, meso- form.



m.p. 134°



m.p. 119.5°

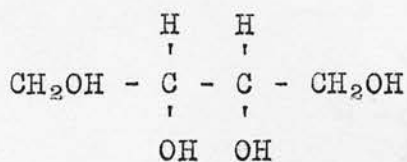
Forst and Zincke (Ann., 1876, 182, 279), in their study of the isomeric hydrobenzoins, found that crystals of isohydrobenzoin, obtained from an ethereal solution, when examined crystallographically, showed marked hemihedrism. In 1897, Erlenmeyer (Ber., 30, 1531) concluded from this fact, that isohydrobenzoin must be separable into right- and left-hand crystals, the solutions of which should display optical activity. This he demonstrated experimentally, by recrystallising isohydrobenzoin from ether. The enantiomorphic crystals separated and were sufficiently well formed to allow of mechanical separation of the right- and left-hand crystals; by dissolving each crystal form individually, and measuring the optical rotation of the solutions, he proved that he had separated the dextro- and laevo-rotatory isomers, and hence that isohydrobenzoin is the racemic modification. It follows that hydrobenzoin is the meso- form.

Hydrobenzoin melts at 134°.

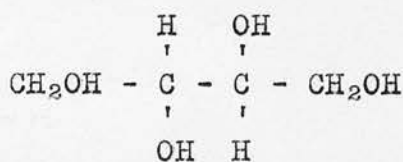
Isohydrobenzoin melts at 119.5°.

Erithrytol, or tetrahydroxybutane, is analogous to

the above example (Griner, Compt. rend., 1893, 117, 554; Maquenne and Bertrand, Compt. rend., 1901, 132, 1566). The inactive meso- form melts at 120° and the resolvable racemic form at 72°.

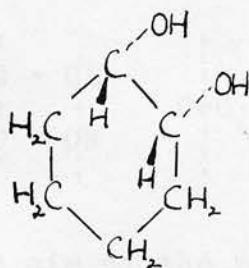


m.p. 120°

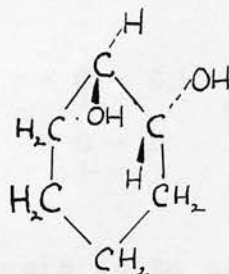


m.p. 72°

The analogy breaks down, however, in the case of 1:2-cyclohexane diols, one of which was resolved by Derx (Rec. trav. chim., 1922, 41, 312), showing that the higher melting form (m.p. 103-104°), possessed the trans- configuration. The cis- modification melts at 98°.



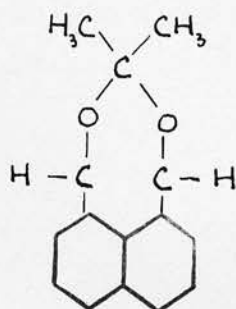
m.p. 98°



m.p. 103-104°

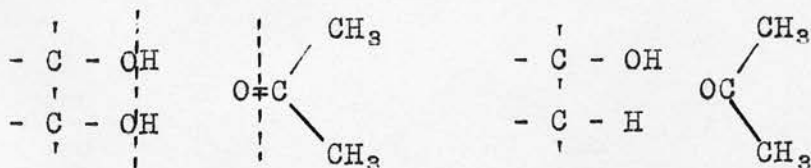
The suggestion, that the trans- configuration probably occurs in the lower melting form of acenaphthylene glycol, has recently been confirmed by the work of Criegee, Kraft and Rank (Ann., 1933, 507, 194). They treated the higher melting form with dry acetone, containing hydrochloric acid gas and anhydrous sodium sulphate, at room temperature. A compound was obtained,

by the condensation of one molecule of the glycol with one molecule of acetone, as was confirmed by analysis, which showed the empirical formula to be $C_{15}H_{14}O_2$.



Similar treatment of the lower melting form left the glycol unchanged.

It is obvious, from an examination of the spatial diagrams, that the cis-form should readily condense with acetone, whereas the reaction is unlikely in the case of the trans-form.



The aim of the present thesis is to establish, by the resolution of the racemic form, which of these acenaphthylene glycols is the cis-, and which the trans-modification.

SUMMARY OF EXPERIMENTAL WORK

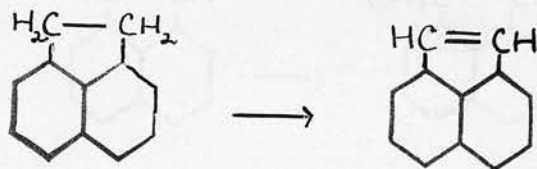
AND

DISCUSSION OF RESULTS.

Preparation of Acenaphthylene Glycol.

As has already been indicated in the introduction, the starting material required for the work, namely acenaphthylene glycol, was obtained from acenaphthene by conversion, first into the unsaturated hydrocarbon acenaphthylene, and thence by addition of bromine into acenaphthylene dibromide, which on hydrolysis gave a mixture of cis- and trans-acenaphthylene glycols.

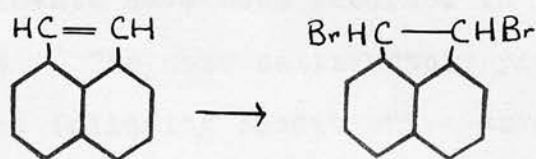
In the first stage, involving the preparation of acenaphthylene, some difficulty was encountered in discovering the best experimental conditions.



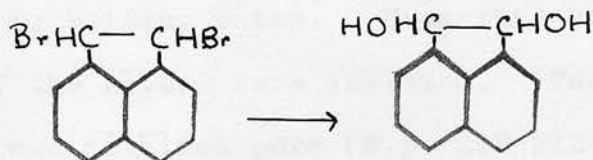
Very little detail on this point is given in the paper of Dziewonski and Rapalski (Ber., 1912, 45, 2491). It was found that the best yields of acenaphthylene were obtained by passing a fairly rapid stream of acenaphthene vapour in a current of carbon dioxide through a silica tube, containing porous tile, at a bright red heat. The emergent vapour consisted of a mixture of acenaphthene and acenaphthylene, very little carbonisation occurring if the conditions were properly regulated. Under the proper conditions the vapours largely condensed to a liquid which eventually solidified; in some cases, however, a "smoke" formed which was very difficult to trap.

The separation of the mixture of acenaphthene and acenaphthylene was effected by the formation of the picrates. Acenaphthene picrate has a melting point of 161-162° while acenaphthylene picrate melts at 201-202° and is much less soluble in alcohol. Thus pure acenaphthylene picrate was obtained by fractional crystallisation from this solvent. The purified acenaphthylene picrate, on decomposition with ammonia, yielded acenaphthylene.

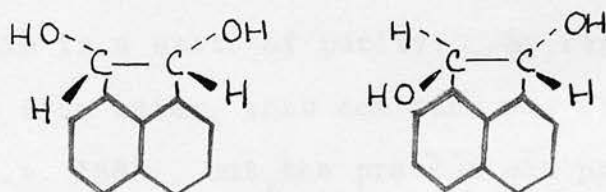
From acenaphthylene the dibromide was prepared by the method of Blumenthal (Ber., 1874, 7, 1093), and



hence, by hydrolysis, the glycol was obtained (Graebe and Jequier, Ann., 1896, 290, 205).



It was considered that, since the glycol existed in two modifications (cis and trans) the dibromide should

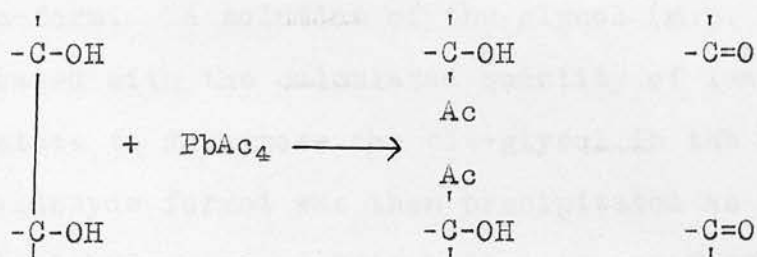


also exist in two isomeric forms. Further purification

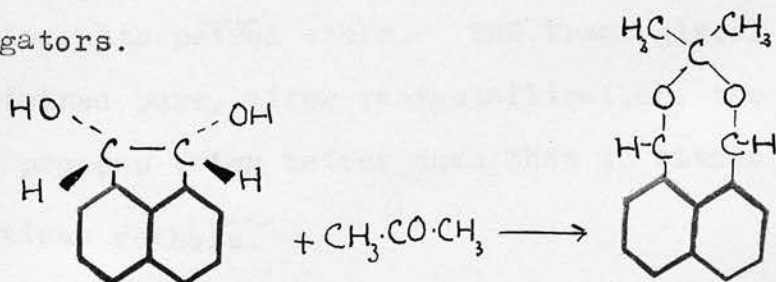
at this stage, therefore, might lead to a reduction of the yield of one form of the glycol, and hence the crude dibromide was hydrolysed without further purification.

Blumenthal prepared the dibromide by bringing acenaphthylene in ethereal solution into contact with a molecular proportion of bromine. To obtain the glycol Graebe and Jequier boiled 1 part of the resulting compound with 100 parts of water. In order to try to increase the yield of glycol, and to reduce the proportion of tar formed, varying conditions were used for the addition of bromine and for the hydrolysis. The results of these experiments have been recorded in tabular form on pp. 42 to 44. The most satisfactory yields were obtained under the following conditions: an ethereal solution of bromine was added slowly to a solution of acenaphthylene, with cooling. The ether was then evaporated off and the crude dibromide, in acetone solution, added slowly to boiling water. From this hydrolysis both forms of the glycol were isolated. The higher melting form was obtained pure (m.p. $212-213^{\circ}$) on boiling with animal charcoal and recrystallisation from aqueous alcohol. The lower melting form (m.p. $158.5-159.5^{\circ}$), however, is much more soluble and is therefore more difficult to obtain in a state of purity. By repeated recrystallisation from water, this compound was obtained almost pure (m.p. 156°), but the process was prolonged and a large proportion of the material was lost.

Criëgee, Kraft and Rank (Ann., 1933, 507, 159) proved that the higher melting glycol was of cis-, and the lower melting of trans-configuration, by their work on the "splitting" of glycols using lead tetra-acetate. They showed that α -glycols decomposed on treatment with lead tetra-acetate in the following manner:



The rates of decomposition of different glycols were found to depend on the configuration of the molecules. The nearer the O-C-C-O atoms approximate to one plane, or the more easily they can take up such a position, the greater is the rate of the reaction. Thus, glycols possessing the cis-configuration are more rapidly attacked than those possessing the trans-structure. In the case of the acenaphthylene glycols they found that the high melting isomeride was of cis-, and the lower melting isomeride of trans-configuration. This was borne out by the preparation of an acetone compound from the high melting form, but not from the lower melting glycol, by the same investigators.



Criegee, Kraft and Rank based a method of purification of trans-acenaphthylene glycol on this decomposition by means of lead tetra-acetate. The crude trans-glycol was purified by recrystallisation until the melting point was raised to about 148° , when, from kinetic experiments, they calculated it contained 18% of the cis-form. A solution of the glycol (m.p. $\approx 148^{\circ}$) was treated with the calculated quantity of lead tetra-acetate to decompose the cis-glycol in the mixture. The dialdehyde formed was then precipitated as the dinitro-phenyl hydrazone. This method of purification was attempted in the present work but was found to be even less economic than purification by repeated recrystallisation and was also a prolonged process.

A better method of purification was evolved based on the formation of an acetone compound of the cis-isomer. The acetone compound was found to be soluble in petrol ether (b.p. $40-60^{\circ}$), in which the acenaphthylene glycols do not dissolve. The crude trans-glycol was accordingly treated with dried acetone containing 1% hydrochloric acid. On removal of the acid in the form of ammonium chloride the solution was evaporated to dryness and the acetone compound of cis-acenaphthylene glycol removed by washing with petrol ether. The trans-glycol was thus obtained pure, after recrystallisation, the yield in this process being better than that in either of the two previous methods.

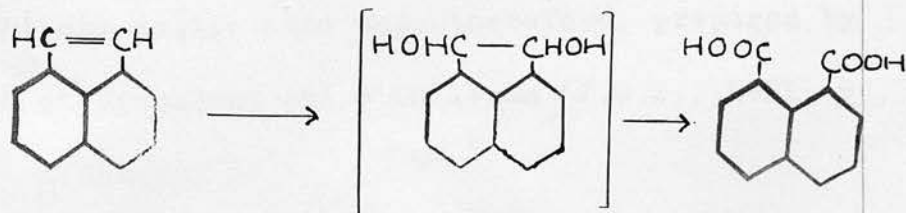
Attempts to prepare Acenaphthylene Glycol from Acenaphthylene by direct Oxidation.

It was decided that it might be possible to oxidise acenaphthylene directly to the glycol without preparing the dibromide. Acenaphthylene, on oxidation, is usually converted to naphthalic acid but it was hoped that, using mild conditions, the reaction might be stopped at the glycol stage.

Oxidation with Potassium Permanganate.

The oxidation was, therefore, carried out using a 2% solution of alkaline permanganate. A solution of acenaphthylene in pyridine was made and the permanganate added in the cold. In this case somewhat more than the calculated amount of permanganate was accidentally used and hence when naphthalic acid was the only product of the oxidation isolated, the experiment was repeated using the calculated weight of permanganate in a 1% solution.

In this experiment only naphthalic acid and acenaphthylene were isolated thus proving that the reaction does not stop at the glycol stage and that this method is therefore useless for the preparation of this intermediate compound.



Oxidation with Hydrogen Peroxide.

Pickard and Yates (J.C.S., 1908, 1680) used Merck's perhydrol (30% hydrogen peroxide) for oxidising unsaturated compounds in the cholesterol series to glycols. It was decided to attempt to apply this reagent to acenaphthylene.

A solution of acenaphthylene in glacial acetic acid was boiled under reflux with hydrogen peroxide but no glycol could be isolated. The experiment was repeated with no greater success.

Resolution of trans-Acenaphthylene Glycol.

Mechanical separation of the optical isomers of trans-acenaphthylene was attempted but without success. A solution ^{in water} of pure trans-acenaphthylene glycol, slightly more than saturated at 15°, was made and allowed to evaporate slowly. Crystals were formed but were insufficiently defined to show any hemihedral facets. In ethereal solution similar results were obtained.

It was then decided to attempt to resolve the glycol by means of *l*-menthoxy acetyl chloride, the reagent introduced so successfully by Read and Grubb (J. Soc. Chem. Ind., 1932, 51, 329 T) in their work on the stereoisomeric menthols.

l-Menthoxy acetic acid was, therefore, prepared by the method of Frankland and O'Sullivan (J.C.S., 1911, 99,

2329) as modified by Rule and Tod (J.C.S., 1931, 1932) and from this, *l*-menthoxy acetyl chloride.

The esterification of the glycol by means of the acid chloride at first presented some difficulties, it being very difficult to obtain a solid ester from the syrup which was produced. Finally, however, the following conditions were found to give satisfactory results.

The glycol was dissolved in pyridine and a slight excess of *l*-menthoxy acetyl chloride added slowly. This mixture was then heated to about 100° for 1 to 2 hours and poured into dilute acid to remove the pyridine. The resulting ester was extracted with ether and washed with sodium hydroxide solution, to remove any unchanged acid, and finally with water. On evaporation of the ether a brownish syrup was obtained in which tiny crystals eventually formed. It was found that crystallisation took place very much more readily if all the pyridine was not removed completely.

After repeated recrystallisation from light petroleum (b.p. 40-60°), the pure ester was isolated. It melted at 113.5-114.5° and was found to have a specific rotation in benzene solution which was unchanged on continued crystallisation.

$$(c = 0.414), \quad [\alpha]_{5461}^{20} = -327^{\circ}.$$

This ester was hydrolysed by heating with sodium hydroxide in aqueous solution. The resulting glycol

was extracted with ether and on recrystallisation from water, was obtained as colourless needles, melting at 158-158.5°.

The original trans-acenaphthylene glycol crystallised in the form of plates and a mixed melting point of the two compounds showed a depression of about 10°.

The rotatory power was tested in various solvents and found to vary with the medium. The behaviour of the compound was of particular interest since the specific rotation, in varying, passed through zero. In solvents of low dipole moment the rotation was positive; in solvents of high dipole moment the rotation was negative; while for ethyl and methyl alcohol, with dipole moments of intermediate values (1.63 and 1.64×10^{18} e.s.u. respectively), the rotation was found to be zero, or too small to be determined.

The number of solvents used was limited by the exceedingly low solubility of the compound in the majority of organic solvents.

Solvent	Concentration (c)	Actual rotation α $l = 4$	$[\alpha]_{5461}^{20}$	Dipole moment of the solvent $\times 10^{18}$ e.s.u.
Benzene	0.08	+0.21°	+66°	0
Chloroform	0.392	+0.81	+52	1.18
Ethyl Alcohol	0.372	0	0	1.63
Methyl Alcohol	0.378	0	0	1.64
Acetone	0.40	-0.39	-25	2.76
Nitrobenzene*	0.324	-0.49	-76	3.98

* In this case a 2 decimeter tube was used.

The rotation was also determined in acetone solution using light of different wavelengths. The dispersion was found to be normal, i.e. the rotatory power increased in magnitude with decrease in the wavelength.

Wave-length λ	Concentration c	$l = 2$ α	$[\alpha]$
(Red) 6560 Å	1.184	-0.43°	-18°
(Green) 5461	1.184	-0.59	-25
(Blue) 4710 *	1.184	(-0.68)	(-29)

* This result was very inaccurate due to the extreme difficulty of reading the polarimeter when using blue light. The results are, however, sufficient to show that the dispersion is normal, i.e. the rotatory power increasing in magnitude as the wave-length decreases.

The preparation of the acetyl derivative of the resolved trans-acenaphthylene glycol was attempted, but

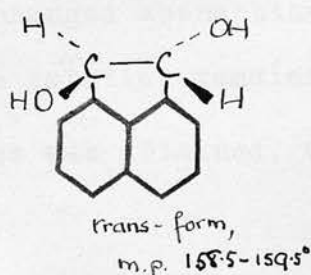
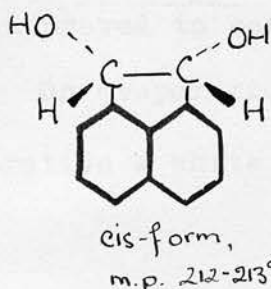
the quantity of glycol available was too small for any satisfactory results to be obtained.

cis-Acenaphthylene glycol was esterified in the same manner as trans-acenaphthylene glycol. On repeated recrystallisation from light petroleum (b.p. 40-60°) a compound was obtained which had a melting point of 40-42°. The specific rotation was tested in benzene solution and found to be

$$(c = 0.418), \quad [\alpha]_{5461}^{20} = -115^{\circ}.$$

Further recrystallisation produced no change in melting point or rotation but the product did not have the appearance of a pure organic compound and the crystals always formed in hard crusts. The analysis figures, however, were in agreement with those calculated for the di-*l*-menthoxy acetate of acenaphthylene glycol.

This compound was hydrolysed by means of alcoholic potassium hydroxide giving an almost quantitative yield of the original cis-acenaphthylene glycol, which had no rotatory power. Taken in conjunction with the resolution of trans-acenaphthylene glycol this establishes the low melting acenaphthylene glycol (m.p. 158.5-159.5°) as the trans-form and the high melting isomeride (m.p. 212-213°) as the cis-form.



Reduction of Acenaphthene Quinone with
Sodium Amalgam.

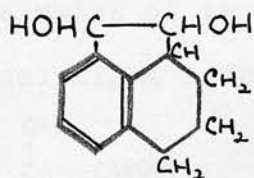
Blount and Weissberger, in a recent paper (J.C.S., 1936, 336), claim to have developed a greatly improved method of preparing cis-acenaphthylene glycol, by reducing acenaphthene quinone with sodium amalgam in an atmosphere of nitrogen. An attempt was therefore made to repeat this preparation. The first attempt was unsuccessful. Acenaphthene quinone, sodium amalgam and absolute alcohol were placed in a round-bottomed flask and stirred mechanically by means of a stirrer fitted with a mercury seal. Nitrogen was ^{led} continuously into the flask, but not below the surface of the liquid and the experiment may have been unsuccessful due to the presence of some oxygen in the nitrogen gas employed. In the next experiment, therefore, nitrogen was led into the liquid and any oxygen present in the nitrogen was removed by first bubbling the gas through an alkaline solution of pyrogallol. The reaction was continued for 24 hours and then glacial acetic acid and water were added to destroy the remaining sodium amalgam. The mercury was removed and, on addition of water to the solution, a precipitate was formed which on removal by filtration proved to contain unchanged acenaphthene quinone. On evaporation of the solution remaining from this filtration a white substance was obtained, which

crystallised in beautiful crystalline plates and melted at 208.5-209°. A mixed melting point with cis-acenaphthylene glycol (m.p. 212-213°) proved that a different compound had been isolated.

The analysis figures suggested that a tetrahydro-acenaphthylene glycol had been prepared. This was confirmed by the preparation of a diacetate, melting at 139-140°, on treatment with acetic anhydride.

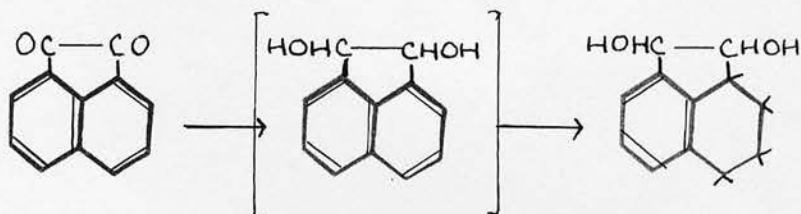
The compound, in chloroform solution, produced no decolourisation of bromine. This shows that all four hydrogen atoms must have entered the same ring in the naphthalene nucleus, as otherwise an unsaturated compound, capable of decolourising bromine, would have been obtained.

Hence the compound must be assigned the constitution of 1.2.3.4-tetrahydro-acenaphthylene glycol.



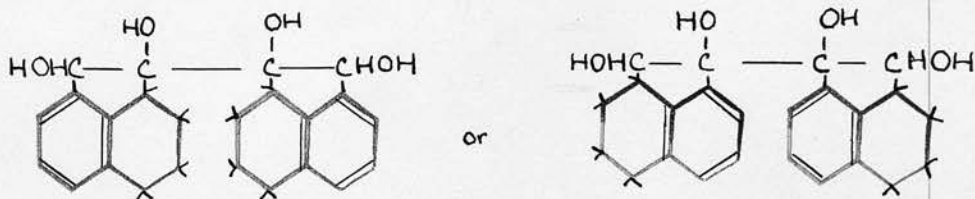
The preparation of this compound was repeated several times, varying the temperature, the proportion of sodium amalgam and the duration of the reduction. No other glycol was, on any occasion, isolated. It is noteworthy that, as in the first successful experiment, unchanged acenaphthene quinone was always found to be present. Thus it appears that, since the reaction was

not complete, the intermediate acenaphthylene glycol when formed is converted immediately into the tetrahydro-acenaphthylene glycol. It is therefore improbable that Blount and Weissberger (*loc. cit.*) actually isolated acenaphthylene glycol in this manner. (See also p. 34)



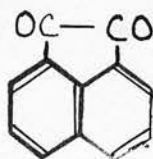
In this paper no melting point of a purified product is quoted, and neither analysis figures nor mixed melting point with *cis*-acenaphthylene glycol are given by the authors.

The melting point of the compound, 209° , obtained in the present work is somewhat higher than was to have been expected in the case of a reduced acenaphthylene glycol. It was at first thought possible that a compound formed by the union of two molecules of tetrahydro-acenaphthylene glycol might have been produced, e.g.

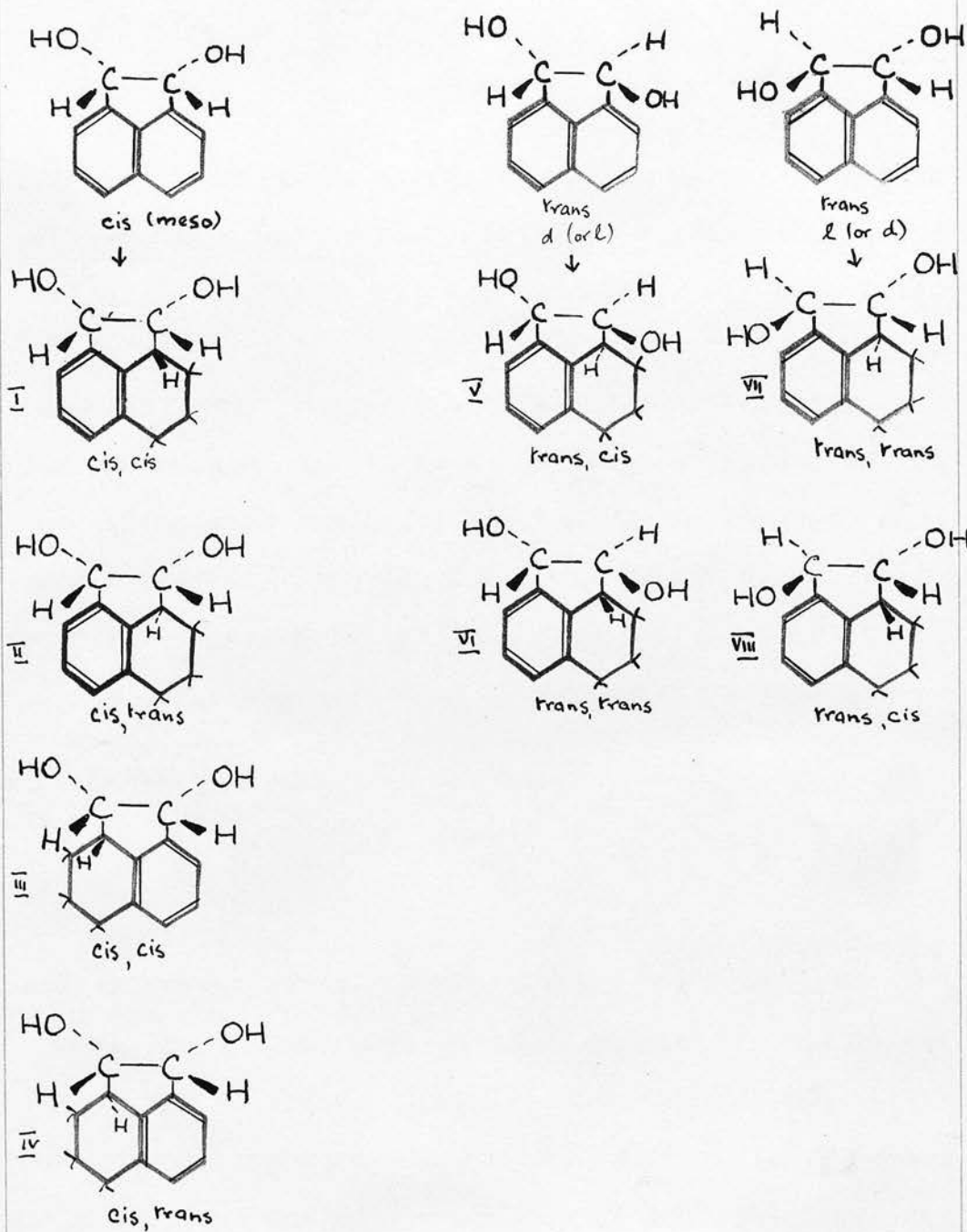


Such compounds are readily formed in the acenaphthylene series and are stable. It is also obvious that the difference between the empirical formula of the tetrahydro-glycol and that of a double compound of the above type is too slight to be apparent in the analysis figures.

SOME REDUCTION PRODUCTS OF ACENAPHTHENE QUINONE.



Acenaphthene Quinone



The molecular weight of the diacetate of the compound was therefore determined and was found to be in agreement with the calculated value for tetrahydro-acenaphthylene glycol diacetate, and not with that of the double compound.

Isomeric Forms of Tetrahydro-Acenaphthylene Glycols.

Examination of the spatial formula of tetrahydro-acenaphthylene glycol shows that there are eight possible isomeric forms (see p.26a). Each of these isomeric forms is a mirror image of another form, thus giving four possible racemates, two derived from cis-acenaphthylene glycol, and two derived from trans-acenaphthylene glycol. In the formulae given the first cis, or trans, refers to the relative positions of the 9- and 10- hydrogen atoms, the second to the relative positions of the 1- and 10- hydrogen atoms.

The following pairs are mirror images:

I and III, II and IV, V and VIII, VI and VII.

This case represents the stereo-isomerism of a compound containing three dissimilar asymmetric atoms. The number of isomers = $2^n = 8$, plus four racemic forms

A: dl cis, cis form; B: dl cis, trans form;

C: dl trans, cis form; D: dl trans, trans form.

The tetrahydro-acenaphthylene glycol prepared from

the quinone must therefore be one of these four forms. It was decided to endeavour to prove whether the hydroxyl groups were of cis- or trans-configuration. The high melting point of the compound ($208.5-209^{\circ}$) seemed to suggest that the compound was of cis-configuration, on analogy with the acenaphthylene glycols. (cis-Acenaphthylene glycol melts at $212-213^{\circ}$; trans-acenaphthylene glycol melts at $158.5-159.5^{\circ}$.) Accordingly the preparation of the acetone compound was attempted but with no success. This was not thought to be sufficient evidence, however, to prove that the compound was of trans-configuration since it has been shown by Böeseken (Rec. Trav. Chim., 1921, 40, 553) that the formation of such complexes takes place only when the hydroxyl groups are in the same plane as the carbon atoms to which they are linked, and on the same side of them.

It is readily seen with the aid of models that, while in the case of cis-acenaphthylene glycol, the hydroxyl groups are coplanar with their attached carbon atoms, in 1.2.3.4-tetrahydro cis-acenaphthylene glycol, this is not the case, the hydroxyl groups being appreciably out of plane.

Attempted Resolution of Tetrahydro-acenaphthylene Glycol.

The tetrahydro-acenaphthylene glycol must, as stated on p. 26, be a racemic compound and therefore, under the proper conditions, should be resolvable. If the hyd-

roxyl groups were of trans-configuration, it was to be expected that, by analogy with the similar trans-acenaphthylene glycol already resolved, the resolution could be brought about by means of the *l*-menthoxy acetates.

Tetrahydro-acenaphthylene glycol was therefore treated with *l*-menthoxy acetyl chloride in pyridine solution, in exactly the same manner as trans-acenaphthylene glycol (see p. 19) and a compound of similar physical properties was obtained. On repeated recrystallisation from petrol ether (b.p. 40-60°), and finally from aqueous alcohol, this compound was obtained in the form of colourless crystalline needles melting at 71-72°. The rotatory power was tested in benzene solution and it was found that,

$$(c = 0.484) \quad [\alpha]_{5461}^{20} = -94^{\circ}.$$

On standing, the oily material left when the petrol ether evaporated off from the original mother liquors, was found to contain clean crystals. These, on separation and recrystallisation, were found to give the same melting point and specific rotation as the final product resulting from repeated recrystallisations, which suggests that probably the original tetrahydro-acenaphthylene glycol had not undergone any optical resolution by being converted into the *l*-menthoxy acetate and fractionated.

Analysis proved that the compound formed was the di-*l*-menthoxy acetate of a tetrahydro-acenaphthylene glycol.

The compound was heated with aqueous sodium hydroxide, but only partial hydrolysis occurred, most of the ester being recovered unchanged. Hydrolysis was then carried out by treatment of the ester with alcoholic potassium hydroxide when an almost quantitative yield of the original tetrahydro-acenaphthylene glycol was obtained. This compound was tested in the polarimeter using solvents of widely differing dipole moments, but was found to have no optical rotatory power.

The fact that no resolution appeared to have been effected suggested that the hydroxyl groups of the racemic tetrahydro-acenaphthylene glycol prepared by reduction of acenaphthene quinone were of cis-configuration, since it might be expected that the trans-compound would be very similar to trans-acenaphthylene glycol and might therefore be resolved under similar conditions. The high melting point of the compound also, by analogy with the acenaphthylene glycols appeared to be further evidence in favour of this view. The fact that no acetone compound can be prepared, is not, as already indicated (see p. 27), sufficient evidence to establish that the compound is of trans-configuration.

Attempted Preparation of Tetrahydro-acenaphthylene Glycol
by Reduction of cis-Acenaphthylene Glycol.

The question of whether the hydroxyl groups in the tetrahydro-acenaphthylene glycol prepared were of cis-

or trans-configuration would be settled if the same compound could be prepared from cis- or trans-acenaphthylene glycol.

The reduction of cis-acenaphthylene glycol was first attempted by means of zinc and potassium hydroxide, but the reaction was not sufficiently vigorous as the unchanged cis-acenaphthylene glycol was recovered quantitatively.

In the next attempt sodium and amyl alcohol were employed. Reduction apparently took place as no unchanged acenaphthylene glycol was recovered, but no pure product could be isolated although the experiment was repeated.

CATALYTIC HYDROGENATION OF ACENAPHTHYLENE GLYCOLS.

It was decided to attempt the catalytic hydrogenation of the acenaphthylene glycols. These experiments were carried out in the apparatus shown on p.81a, with hydrogen under 2-3 atmospheres pressure and using platinum oxide or palladium precipitated on barium sulphate as catalysts.

Hydrogenation of cis-Acenaphthylene Glycol.

Attempts to hydrogenate cis-acenaphthylene glycol were made under various conditions. The first solvent used was glacial acetic acid, the catalyst being plat-

inum oxide, but after about one third of the desired amount of hydrogen had been absorbed, further absorption became very slow and the experiment was discontinued.

In the next attempt the same solvent was used but on this occasion heat was applied and hydrochloric acid and ferric chloride added to accelerate the reaction. Absorption was, in this case also, arrested and the hot acid was found to have attacked the copper valves of the apparatus. On addition of water to the acid solution an orange coloured oil was obtained; this may have been due to the occurrence of acetylation.

It was, therefore, decided to use alcohol as solvent and all the following hydrogenations were carried out in this manner with heating to 50°.

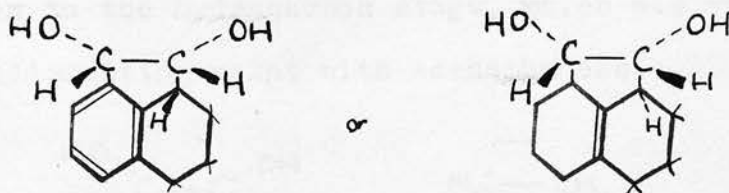
In the first experiment using alcohol as a solvent, the catalyst was again platinum oxide and a few drops of hydrochloric acid and ferric chloride were added to accelerate the reaction. When the required amount of hydrogen (4 atomic proportions) had been absorbed the experiment was stopped. On addition of water to a test portion an oil appeared to be formed and therefore the solution was evaporated slowly to small volume. A solid product was deposited, which appeared to be a mixture. It was thought that some glycol chloride might have been formed from the hydrochloric acid present and hence this solid material was boiled with water to hydrolyse any such material. An oil A was formed and sep-

arated off.

On evaporation of the filtrate a white crystalline substance was obtained, which on recrystallisation was found to melt at $92.5-93.5^{\circ}$. Analysis and the formation of a diacetate (m.p. $121-121.5^{\circ}$) on treatment with acetic anhydride showed this compound to be a tetrahydro-acenaphthylene glycol. It is, however, not identical with the product obtained by the chemical reduction of acenaphthene quinone.

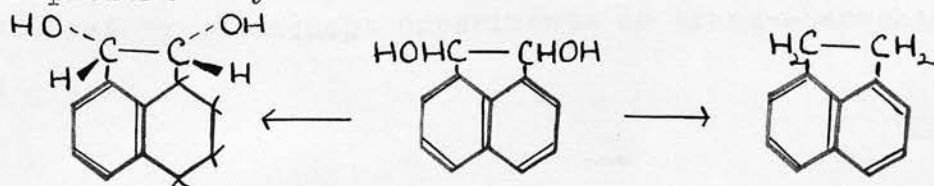
A solution, in chloroform, produced no decolourisation of bromine this proving all four hydrogen atoms had entered the same ring in the naphthalene nucleus.

This compound must therefore be 1.2.3.4-tetrahydro-cis-acenaphthylene glycol.



From the oil A a small quantity of a substance melting about 92° , but distinct from the glycol already isolated, was obtained. The amount was too small to allow of identification of the compound at this stage, but it was later proved to be acenaphthene.

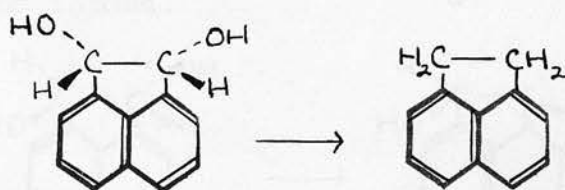
The reactions occurring are therefore probably to be represented by the following scheme:



An attempt to repeat this experiment in order to obtain more of the unidentified product was unsuccessful. This may have been due to some unknown impurity inhibiting the reaction of the catalyst. Since palladium catalyst is less easily poisoned it was used instead of platinum oxide in the next experiment.

In this case a good yield of a compound, which was proved by mixed melting point to be identical with the unidentified compound A in the previous experiment, was obtained.

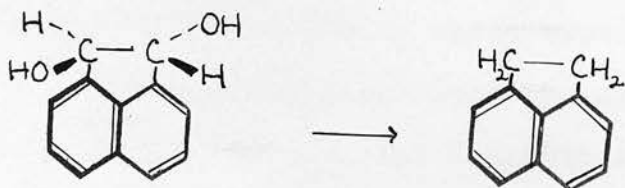
It was at first assumed that a different tetrahydro cis-acenaphthylene had been isolated, but all efforts to prepare an acetyl derivative were unsuccessful. This suggested that the 1:8-bridge had undergone complete reduction to the hydrocarbon stage, which was verified by a mixed melting point with acenaphthene.



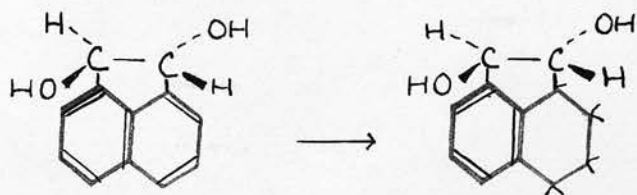
Thus it is evident that the catalysts have a specific effect, hydrogenation taking place preferentially at the hydroxyl groups, when palladium is used, whereas, using platinum oxide as a catalyst, reduction within the naphthalene nucleus takes place more readily. This was borne out by subsequent experiments on trans-acenaphthylene glycol.

Catalytic Hydrogenation of trans-Acenaphthylene Glycol.

Hydrogenation of trans-acenaphthylene glycol using palladium catalyst led to the formation of acenaphthene only.

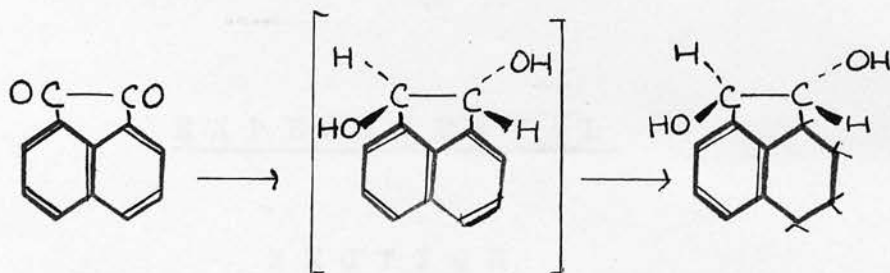


Hydrogenation of trans-acenaphthylene glycol using platinum catalyst resulted in the production of a substance which crystallised in the form of plates and melted at 207-208°. A mixed melting point identified this compound as the 1.2.3.4-tetrahydro-acenaphthylene glycol prepared by the reduction of acenaphthene quinone with sodium amalgam. In this case no acenaphthene appeared to be formed.



The preparation of this compound from trans-acenaphthylene glycol proves it must be 1.2.3.4-tetrahydro-trans-acenaphthylene glycol. This fact provides additional support for the suggestion that Blount and Weissberger (J.C.S., 1936, 336) (see p. 25) could not have isolated cis-acenaphthylene glycol, since the melting

point of the (crude) product obtained by them is quoted as "above 160°". The melting point of cis-acenaphthylene glycol is 212-213°, that of trans-acenaphthylene glycol 158.5-159.5°. The intermediate acenaphthylene glycol formed in the chemical reduction must have been the lower melting trans-form which cannot be isolated under the experimental conditions employed, because it is rapidly converted into the trans-tetrahydro derivative.



EXPERIMENTAL

SECTION.

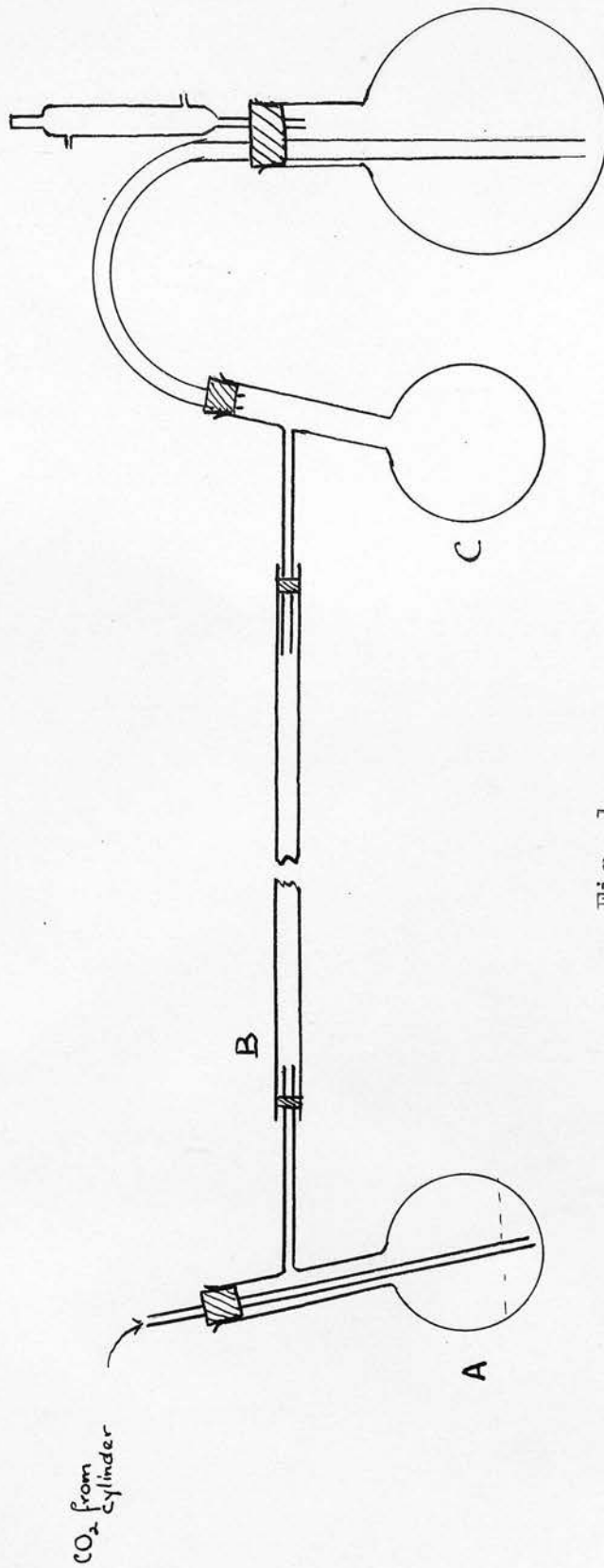
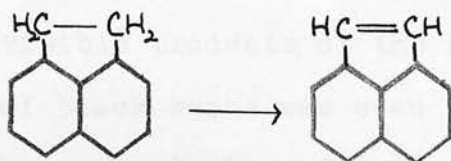


Fig. 1.

Preparation of Acenaphthylene from Acenaphthene.

Reference: Dziewonski and Rapalski, Ber., 1912, 45,2491.



Acenaphthylene was prepared by the method used by Dziewonski and Rapalski, viz., acenaphthene vapour was passed through a red-hot silica tube in an atmosphere of carbon dioxide. The acenaphthene was heated in a distilling flask (A), the side tube of which was fitted into a silica tube (B) by means of a stopper of asbestos paper. At the other end was another distilling flask (C), similarly fitted into the silica tube, and to this flask by means of a U-tube between the necks was connected a large flask cooled in ice and fitted with a double surface condenser. Carbon dioxide, from a cylinder was led by means of a tube to the foot of the flask, A, containing acenaphthene and the silica tube was heated in a furnace. By experiment it was found that the yield was increased when the silica tube was packed with pieces of porous plate. Finally the best conditions were found to be as follows:

- 1) Acenaphthene in the flask heated until it was boiling gently;
- 2) silica tube heated to fairly bright red heat;
- 3) a sufficiently rapid flow of carbon dioxide from the cylinder.

If the rate of flow of carbon dioxide was insufficient, charring took place and, instead of a yellow or reddish smoke emerging from the silica tube, there were either no visible products of the reaction, or a small quantity of black smoke was seen in the receiving vessels. If the rate of flow of carbon dioxide was too rapid, or the temperature too low, the acenaphthene came over unchanged.

It was also found that the acenaphthylene-acenaphthene mixture tended to come over in the form of a solid smoke, which was very difficult to condense. With regulation of the heating and of the rate of flow of carbon dioxide and acenaphthene, however, it was found that the mixture could be obtained in such a form that the main portion of it condensed in the first receiving vessel.

The mixture in the receiving vessels, which was frequently coloured red due to the presence of some other hydrocarbon, consisted mainly of acenaphthene and acenaphthylene.

Separation of Acenaphthene and Acenaphthylene.

The acenaphthylene was separated from the unchanged acenaphthene by the formation of the picrates and fractional recrystallisation.

For this purpose the mixture was dissolved in alcohol and filtered, while hot, to remove any carbon present. The clear solution was then treated with a solution

containing the weight of picric acid corresponding to the weight of hydrocarbon mixture used. Acenaphthene formed an orange-coloured picrate (m.p. 161-162°) while acenaphthylene picrate was a brown substance (Blumenthal, (Ber., 1874, 7, 1093) and Behr and van Dorp (Ber., 1873, 6, 753) quote it as yellow needles) crystallising in long needles and melting at 201-202°, which is much less soluble in alcohol than is acenaphthene picrate. Thus, by fractional crystallisation from alcohol, pure acenaphthylene picrate was obtained.

Decomposition of Acenaphthylene Picrate.

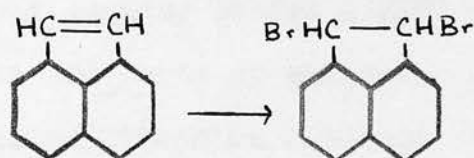
Acenaphthylene picrate was decomposed by treatment with ammonia. Concentrated ammonia mixed with an equal volume of water was heated and poured on to the picrate, the mixture stirred and allowed to stand for a short time before filtering. The acenaphthylene picrate was thus decomposed giving acenaphthylene, which is insoluble in water, and ammonium picrate, which readily dissolves in water. The ammonium picrate, which was in the filtrate, was treated with sulphuric acid in order to recover the picric acid. The acenaphthylene, from which the ammonium picrate had been filtered off, was repeatedly subjected to the same treatment, until the filtrate showed no yellow colouration. The yellowish brown amorphous solid thus obtained was dissolved in alcohol, boiled with animal charcoal, filtered while hot and the acenaphthylene

obtained as yellow plates, which, after a further recrystallisation from alcohol had the melting point of the pure substance, 92-93°.

The highest yield of acenaphthylene obtained was 47.5% of the theoretical, 19 gms. of acenaphthene giving 26 gms. of pure acenaphthylene picrate, which on decomposition and recrystallisation of the resulting product, gave 9 gms. of pure acenaphthylene.

Preparation of Acenaphthylene Dibromide.

Reference: Blumenthal, Ber., 1874, 7, 1093.

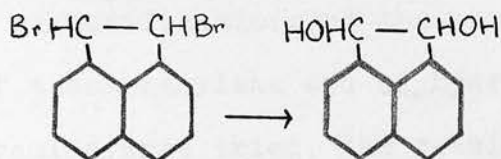


Blumenthal prepared the dibromide by bringing molecular proportions of bromine into contact with an ethereal solution of acenaphthylene. Accordingly, 14 gms. of acenaphthylene was dissolved in ether and 14 gms. of bromine added, a few drops at a time, with shaking. When the excess of ether was evaporated off, a brownish crystalline mass was left, which was recrystallised from benzene and eventually absolute alcohol. A yield of 3 gms. of the dibromide, which crystallised as white plates melting at 118°, was thus obtained (Blumenthal quotes the melting point as 121-123°). On evaporation of the mother liquors 15 gms. of a crude brownish dibromide, and finally a further quantity of a brown oil, was obtained. Since acenaphthylene glycol exists as two cis- and trans- isomers, it was thought there might

be two forms of the dibromide also and that in the process of purification much of the lower melting isomer would be lost. It was therefore decided to hydrolyse the dibromide directly to the glycols, without any purification at this stage.

Preparation of Acenaphthylene Glycols.

Reference: Graebe and Jequier, Ann., 1896, 290, 205.



Graebe and Jequier boiled 1 part of acenaphthylene dibromide with 100 parts of water for one hour. The three portions of dibromide, obtained in the last experiment, were treated thus without further purification. A large proportion of tar formed in each case and was removed by repeated filtration while hot. On cooling, white crystals of the cis-glycol were deposited, filtered off and found to melt at about 190°. On recrystallisation from aqueous alcohol with the use of animal charcoal, this compound was obtained in the form of long, silky, white needles, melting at 212-213°. Graebe and Jequier, and Ewan and Cohen (J.C.S., 1889, 55, 578) quote the melting point as 204°; Criegee, Kraft and Rank (Ann., 1933, 507, 194) record 209-210°. The mother liquors from the hydrolysis of the dibromide were evaporated down, when the trans-glycol deposited in the form of white crystalline plates, melting about 145°. Difficulty was experienced in obtaining the last portion of

this more soluble glycol as, beyond a certain point, evaporation of the aqueous solution produced tarring. This was apparently due to the presence of hydrogen bromide from the hydrolysis of the dibromide, since, when purified, the glycol remained stable even on evaporation to dryness. The melting point of the pure trans-acenaphthylene glycol is stated to be 159.5° and various methods of purification were examined.

A number of modifications of the conditions of the bromination of acenaphthylene and of hydrolysis of the resulting dibromide were tried, the results of which are listed in tabular form on pp. 42 to 44.

Finally the most satisfactory method was found to be as follows:

8 gms. of acenaphthylene was dissolved in ether and cooled to -10° by means of an ice and salt mixture. 1.2 gms. (4 ccs.) of bromine was dissolved in ether and added slowly from a dropping funnel, with shaking. Some greyish precipitate was formed and this and the ethereal solution were transferred to a separating funnel and the ether evaporated off with a stream of air. By this method, a large quantity of hydrogen bromide, formed during the bromination, was also removed. The solid was then dissolved in acetone and the solution gradually run into boiling water (100 parts of water to 1 part of acenaphthylene dibromide, i.e. 200 parts of water to 1 part of acenaphthylene), and boiled for one hour. The tar formed was filtered off from the hot solution and, on cooling, the cis-acenaphthylene was

Vol. of Br ₂ /gm. Acenaph- thylene	Conditions of addition of Br ₂	Conditions of Hydrolysis	cis-Glycol		trans-Glycol		
			Wt./gm. of ace- naphthyl- ene	m.p.	Wt./gm. of ace- naphthyl- ene	m.p.	Calc. wt. of m.p. 157°
0.33 cc. (Calc. vol.)	Dropped into eth- ereal soln. of acenaphthylene.	Boiled for 1 hour.	0.19 gm.	197°	0.14 gm.	142-144°	0.07 gm.
0.33	Passed, as vapour, into soln. of ace- naphthylene in nitrobenzene at 100°.	Steam distilled to remove nitro- benzene, then boiled 1 hour.	0.2	195°	0.1	144-147°	0.05
0.33	Ditto at 30°	Ditto.	very little	180-197°	neglig- ible amount	—	—
0.33	Passed, as vapour, into benzene soln. at 30° and benzene evaporated off at about 30°.	Boiled for 1 hour.	0.08	198°	0.07 gm.	144-145°	0.03
0.33	Acenaphthylene dis- solved in alcohol, hot water added to give a suspension. Br ₂ mixed with wat- er and dropped into mixture.	Diluted with water and boiled for 1 hour.	0.06	165-175°	0.06	138-145°	0.02

Vol. of Br ₂ /gm. Acenaphthylene	Conditions of addition of Br ₂	Conditions of Hydrolysis	cis-Glycol		trans-Glycol		
			Wt./gm. of ace- naphthyl- ene	m.p.	Wt./gm. of ace- naphthyl- ene	m.p.	Calc. wt. of m.p. 157°
Slight excess Br ₂	Acenaphthylene dissolved in ether, cooled to -10° and Br ₂ passed in as vapour.	Boiled for 2 hours.	0.39 gm.	185-190°	0.24 gm.	138-142°	0.10 gm.
			0.24	195°	0.18	144°	0.08
0.5 cc.	Acenaphthylene dissolved in ether and cooled to -10° Br ₂ passed in as vapour.	Heated gently for 1 hour, then boiled for 1 hour.	0.275	190-194°	0.195	137-142°	0.08
0.4	Br ₂ passed, as va- pour, into ether- eal soln. at -10°. Soln. halved and ether evaporated.	1) Half heated gently for $\frac{1}{2}$ hr. then boiled for 2 hours. 2) Other half dis- solved in acetone and added, from dropping funnel, to boiling water. Boiled for $1\frac{1}{2}$ hrs.	0.38	192°	0.14 0.06	141-142° 147-150°	0.09

Vol. of Br ₂ /gm. Acenaph- thylene	Conditions of addition of Br ₂	Conditions of Hydrolysis	cis-Glycol		trans-Glycol		
			Wt./gm. of ace- naphthyl- ene	m.p.	Wt./gm. of ace- naphthyl- ene	m.p.	Calc. wt. of m.p. 157°
0.5 cc.	Br ₂ passed, as vap- our, into ethereal soln. of acenaph- thylene. Ether evaporated off.	Dissolved in ace- tone, dropped into water mechanically stirred at about 60°. Boiled for 2 hrs.	0.4 gm.	194-197°	0.22 gm.	130° (approx.)	0.09 gm.
0.5	Br ₂ , in ether, dropped into soln. of acenaphthylene in ether at -10°. Ether evaporated off.	Dissolved in ace- tone and run into boiling water. Boiled for 1 hour.	0.35	190-195°	0.26	140-144°	0.11

Note: In the last column the weights of pure glycol are those which could be obtained by removing the remaining cis-glycol by conversion into the acetone compound (see p. 52).

obtained. Yield, 2.8 gms; m.p. 190-195° (28% of the theoretical) which on purification gave 1.7 gms., m.p. 207-208°. (17% of the theoretical) The mother liquors from the hydrolysis on evaporation gave 2.2 gms. (22% of the theoretical) of trans-acenaphthylene glycol melting at 140-144° which, on purification, gave 0.88 gms. (9% of the theoretical yield) m.p. 157°. These yields correspond to a total of 26 per cent of the pure cis- and trans-glycols. Preparations recorded in the literature give no actual yields.

Attempt to prepare Acenaphthylene Glycols from Acenaphthylene by direct Oxidation with Potassium Permanganate.

1 gm. acenaphthylene.

2.8 gms. potassium permanganate.

The acenaphthylene was dissolved in pyridine and the potassium permanganate added gradually, in the cold, in a 2% alkaline solution. Reaction occurred immediately and the mixture was left to stand overnight. The brown precipitate was then filtered off, and this, on boiling up with water, filtering and cooling of the solution, gave no deposit of glycol.

The original filtrate, which was brownish in colour, was treated with hydrogen peroxide. Much effervescence occurred and the solution became colourless. This solution was allowed to stand for some time, filtered and acidified with hydrochloric acid, and, after standing

white needles crystallised out and were filtered off and found to melt at 265° . The filtrate, on extraction with ether, yielded more of this compound which is undoubtedly naphthalic acid the melting point of which is 266° , (confirmed by mixed melting point).

As part of the oxidation in the above experiment might have been due to the action of the hydrogen peroxide, and as an excess of potassium permanganate (twice the calculated amount) was used, it was decided to modify the method slightly.

0.5 gm. acenaphthylene

0.7 gm. potassium permanganate.

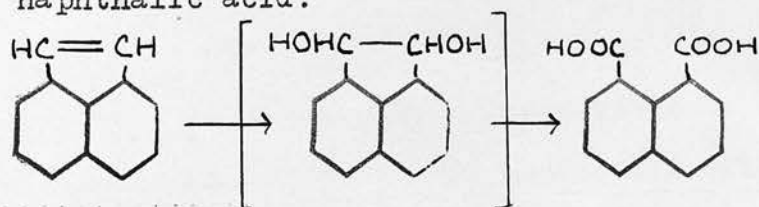
The acenaphthylene was dissolved in pyridine and the calculated weight of permanganate added gradually, in the cold, in a 1% alkaline solution. On standing and filtering off of the precipitate as before, a brownish solution was obtained. This solution was acidified with hydrochloric acid and the resulting precipitate filtered off and found to consist of yellow plates, melting at 88° and thus appeared to be unchanged acenaphthylene.

The solution was then extracted with ether and a few needles, slightly yellow in colour, obtained on evaporation of the ether. Some yellowish needles also appeared in the aqueous solution on standing overnight. They were filtered off and found to melt at 260° ; so

were obviously not either of the acenaphthylene glycols, which melt at 159° and 212° respectively, but must have been naphthalic acid, as in the previous experiment.

The filtrate, on evaporation to dryness and extraction with ether, gave no residue on evaporation of the ether.

This method is therefore of no value for the preparation of the glycols since much of the original acenaphthylene was recovered together with the oxidation product, naphthalic acid.



Attempt to prepare Acenaphthylene Glycols from Acenaphthylene by direct Oxidation with Hydrogen Peroxide.

Merck's "perhydrol" (30% hydrogen peroxide) was used by Pickard and Yates (J.C.S., 1908, 1680) for oxidations in the cholesterol series, in which an unsaturated compound was converted into a glycol. It was decided to apply this reagent to acenaphthylene.

- 1 gm. acenaphthylene
- 12 ccs. glacial acetic acid.
- 3 ccs. perhydrol.

The above mixture was boiled under reflux for two hours on a steam bath. Water was added and a dark brown precipitate and yellowish suspension obtained. The

precipitate was filtered off. In a melting point tube this substance softened about 80° and melted about 100° . On boiling for an hour with water, some tar was left and the solution turned yellow. The tar was filtered off and, on cooling, a curdy yellow precipitate, which was not the glycol, was obtained. This substance might still have been the glycol acetate and was therefore boiled with potassium hydroxide for one hour. The solution darkened and a small quantity of a black precipitate was deposited, but no glycol could be detected.

A further attempt to obtain the glycols by similar treatment, but by heating for six hours, met with no greater success.

Purification of trans-Acenaphthylene Glycol
by Recrystallisation.

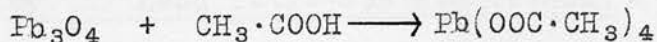
The trans-glycol was purified by repeated recrystallisation from water.

2.8 gms., melting at about 140°, on recrystallisation gave 2.1 gms. of melting point 149-151° which, on further recrystallisation finally yielded 0.98 gm., melting at 156°. This corresponds to a yield of 46% of the weight of melting point 148-150° (for comparison with the other methods used). The pure trans-glycol melts at 159-159.5°.

Preparation of Lead Tetra-acetate.

Reference: Fieser's Experiments in Organic Chemistry, p. 322.

Dimroth, Ber., 1923, 56, 1375; modified by Hellmuth, Dissertation, Wurzburg, 1930.



100 ccs. Glacial acetic acid.

80 ccs. acetic anhydride.

130 gms. powdered red lead (Pb_3O_4)

The glacial acetic acid and acetic anhydride were placed in a wide necked flask, heated to 55° and stirred

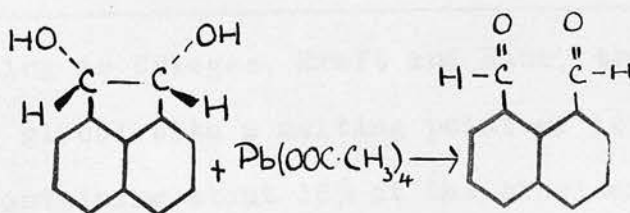
mechanically while the red lead was added in 4 gm. portions, waiting each time till the colour disappeared. The temperature of the mixture was kept between 50° and 80° and near the end of the experiment 25 ccs. of glacial acetic acid and 20 ccs. of acetic anhydride were added, to compensate for the loss due to evaporation.

In the course of the experiment the solution became brown, probably due to the formation of lead peroxide, and some crystals of lead tetra-acetate separated out. On standing, more crystals were deposited and were filtered off. The precipitate was dark in colour but on recrystallisation from acetic acid gave colourless crystals. These were dried in a vacuum desiccator over concentrated sulphuric acid and were recrystallised again from glacial acetic acid.

Yield, 32 gms.

Purification of trans-Acenaphthylene Glycol
by the Lead Tetra-acetate Method.

Reference: Criegee, Kraft and Rank, Ann., 1933, 507, 194.



0.56 gm. Glycol, m.p. 149-152°*

0.09 gm. lead tetra-acetate.

The glycol was dissolved in glacial acetic acid and a solution of lead tetra-acetate, in the same solvent, added. The tetra-acetate reacted almost instantaneously and the dialdehyde so formed was then precipitated as the hydrazone with the calculated amount (0.07 gm.) of 2:4-dinitrophenyl hydrazine. After 15 minutes double the quantity of water was added and the hydrazone filtered off. After removal of the lead by precipitation as the sulphide, the filtrate was recrystallised from water with the use of animal charcoal.

Yield of pure glycol, 0.2 gm. (36% yield); m.p. 159-159.5° (Criegee, Kraft and Rank quote 158.5-159.5°)

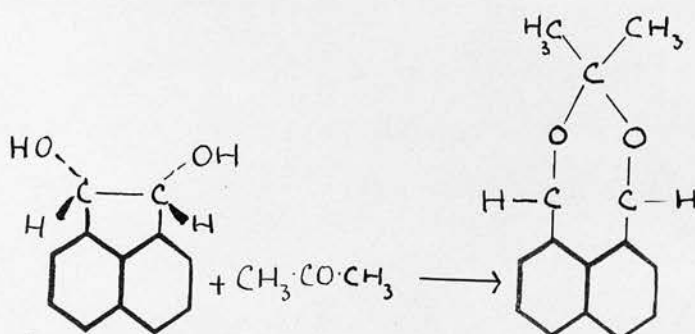
The quantities of reagents used in this experiment were somewhat less than those calculated assuming 18% of the cis-form present in the acenaphthylene glycol, but appear to have given quite satisfactory results. No better results were obtained when this experiment was repeated with the calculated quantities of the reagents.

* According to Criegee, Kraft and Rank, trans-acenaphthylene glycol with a melting point of 147-149° is a mixture containing about 18% of the cis-isomer.



Purification of trans-Acenaphthylene Glycol by
removing the cis-isomer in the form of its
Acetone Compound.

Reference: Criegee, Kraft and Rank, Ann., 1933, 507, 195.



0.41 gm. Glycol m.p. 148-150°

5 ccs. dried acetone containing 1% HCl.

The glycol, suspended in the acetone, was allowed to stand at room temperature for 24 hrs. with some added anhydrous sodium sulphate to act as a drying agent. Enough dried acetone was then added to bring any undissolved glycol into solution and dry ammonia was passed in to neutralise the hydrochloric acid. The solution was then filtered from inorganic salts and the excess of acetone evaporated off. The acetone compound of the cis-glycol was soluble in petrol ether (b.p. 40-60°), which does not dissolve the glycol. The residue from the acetone solution was transferred to a flask and heated with petrol ether, decanted and filtered. This

was repeated twice and the solid dried. 0.33 gm. of trans-glycol m.p. 150-152° was obtained, which, on recrystallisation from water, gave 0.23 gms. (56% yield) m.p. 156.5-157°.

Examination of the Crystals of trans-Acenaphthylene Glycol for mechanical Separation into optical Isomers.

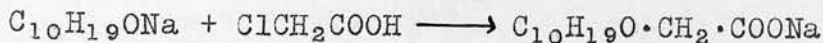
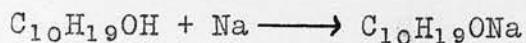
An aqueous solution of the pure glycol (m.p. 159.5°), was made which was slightly more than saturated at room temperature. On leaving this solution to evaporate slowly, crystals were formed, but were insufficiently defined to be examined for hemihedral facets. The majority of the crystals appeared to be flat square plates.

A few drops of the solution were allowed to evaporate on a microscope slide, but, here again, the definition of the crystal forms was insufficient for it to be seen if facets were present.

An ethereal solution was left in a dish, covered with a watch glass to prevent rapid evaporation. Again the crystals seemed to be flat squares, too small and ill-formed to show any hemihedral facets.

Preparation of *l*-Menthoxo Acetic Acid.

l-Menthoxo acetic acid was prepared according to the method of Frankland and O'Sullivan (J.C.S., 1911, 99, 2329) as modified by Rule and Tod (J.C.S., 1931, 1932).



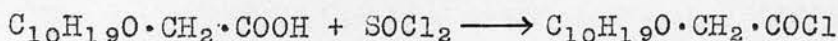
l-Menthol, 312 gms. (2 moles) was placed in a distilling flask with stoppered side tube and fitted with a long air condenser. It was heated on an oil bath to 150°, and 12 gms. of sodium ($\frac{1}{2}$ mole) was added in small pieces through the condenser. When all the sodium was dissolved the excess menthol was distilled off under diminished pressure in a current of hydrogen. The sodium menthoxide, which remained in the flask, was dissolved in 200 ccs. of sodium dried benzene and the solution transferred to a litre round-bottomed flask. A solution of 20 gms. of chloracetic acid in 200 ccs. of sodium dried benzene was then added gradually and the mixture heated on an oil bath at 110-115° for 24 hours. The sodium menthoxo acetate was washed out with water, the aqueous solution acidified with sulphuric acid and

the free menthoxy acetic acid extracted with ether. The ether extract was dried and concentrated to a syrup which was distilled under reduced pressure. The yield of crude product was 49 gms., b.p. 150-190°/11 mm., which was redistilled giving 37 gms. b.p. 171-178°/9 mm. (84% of the theoretical). The rotation of a sample of this was tested in methyl alcohol solution and it was found that

$$(c = 2.696) \quad [\alpha]_{5461}^{20} = -108.7^{\circ}.$$

Tod (Thesis, Edinburgh, 1931, 78) records - 108.6°.

Preparation of *l*-Menthoxy Acetyl Chloride.



20 gms. *l*-Menthoxy acetic acid

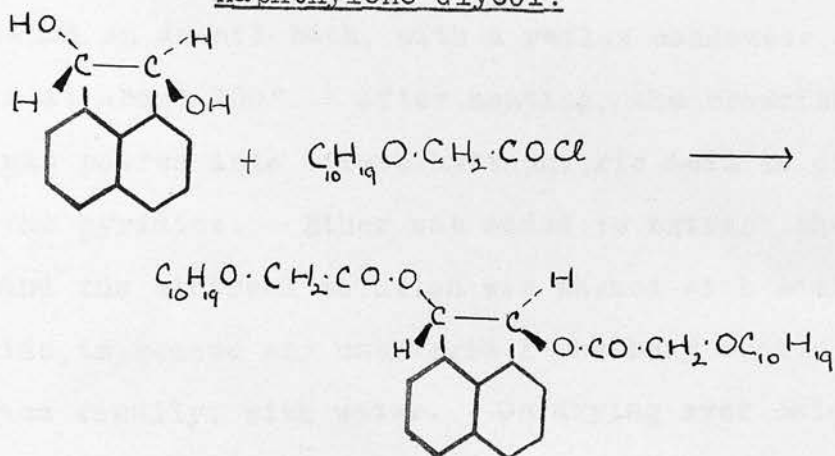
40 ccs. thionyl chloride.

l-Menthoxy acetyl chloride was prepared by heating the acid with thionyl chloride on an oil bath at 100° for an hour, or until no further fumes were evolved. The excess of thionyl chloride was removed by distillation under reduced pressure, finally with addition of a little benzene. The acid chloride was then distilled under reduced pressure. (21 gms., b.p. 128-137°/8 mm.) Distillation was repeated and a yield of 13 gms., b.p.

130-134°/9 mm. (82% of the theoretical) was obtained.

Resolution of trans-Acenaphthylene Glycol.

Preparation of the di-*l*-Menthoxo Acetate of trans-Acenaphthylene Glycol.



The esterification was attempted under different conditions, varying the proportion of *l*-menthoxy acetyl chloride, and the time of heating. Benzene was tried as a solvent and the esterification was also attempted in the absence of a solvent (in both these cases sufficient pyridine was added to remove the free hydrochloric acid produced in the reaction). Finally the most satisfactory conditions were found to be the following:

- 2 gms. trans-acenaphthylene glycol, m.p. 155°.
- 20 ccs. pyridine, dried over sodium hydroxide.
- 7 gms. *l*-menthoxy acetyl chloride.

The glycol was dissolved in the pyridine and the *l*-menthoxy acetyl chloride added gradually. A red colouration appeared and a white precipitate formed, with the development of heat. (These changes were also noted when *l*-menthoxy acetyl chloride was added to pyridine in the absence of any glycol.) The mixture was heated on an oil bath, with a reflux condenser, for an hour at about 100°. After heating, the brownish solution was poured into dilute hydrochloric acid to dissolve the pyridine. Ether was added to extract the ester and the ethereal solution was washed with sodium hydroxide, to remove any unchanged *l*-menthoxy acetic acid, and finally, with water. On drying over calcium chloride and evaporation of the ether a brownish, very sticky, oil was obtained from which, eventually, a mass of very small crystals separated. It was found that crystallisation took place much more rapidly if the pyridine was not completely removed.

6.92 gms. of the solid were obtained. For the first few recrystallisations the product was very sticky, but, after recrystallisation four times from petrol ether (b.p. 40-60°) this gave 1.03 gms. of white needle-like crystals which melted at 113.5-114.5°. The rotatory power of this compound was tested in benzene solution, using the mercury green line ($\lambda = 5461 \text{ \AA}$), and it was found that,

$$(c = 0.414), \quad [\alpha]_{5461}^{20} = - 327.3^{\circ}.$$

On recrystallisation from petrol ether the melting point and rotatory power remained unchanged, the specific rotation being found to be

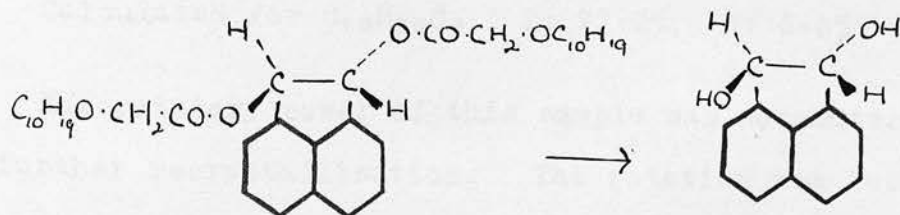
$$(c = 0.39), [\alpha]_{5461}^{20} = -326.9^{\circ}.$$

Analysis:

Found, C: 74.6%, H: 8.7%.

Calculated for $C_{36}H_{50}O_6$, C: 74.7%, H: 8.7%.

Hydrolysis of the di-*l*-Menthoxo Acetate of trans-Acenaphthylene Glycol.



0.5 gm. di-*l*-Menthoxo acetate of trans-acenaphthylene glycol.

10 ccs. 10% sodium hydroxide.

This mixture was heated on the steam bath. The ester did not dissolve but, at the end of an hour, a little oil was seen, showing that hydrolysis was taking place. A dark bluish colour was also produced. A few ccs. of alcohol were added to dissolve the ester and so increase the rate of hydrolysis. The bluish colour vanished, but reappeared on further heating. After

two hours heating hydrolysis was complete. The resulting glycol was extracted with ether, the ether solution being colourless, the colour remaining in the aqueous layer. On evaporation of the ether, 0.16 gm. (quantitative yield) of a glycol, which crystallised as white needles melting at 156-158°, was obtained. This was recrystallised from water giving a pure sample, m.p. 158-158.5°. The mixed melting point of this substance with the unresolved trans-acenaphthylene glycol (m.p. 158°) was found to be 149-152°.

Analysis:

Found, C: 77.4%, H: 5.43%.

Calculated for $C_{12}H_{10}O_2$, C: 77.2%, H: 5.6%.

The rotatory power of this sample was not altered by further recrystallisation. The rotation was tested in various solvents for the mercury green line ($\lambda = 5461 \text{ Å}$) using a 4 decimeter tube.

Solvent	Concentration (c)	Actual rotation α $l=4$	$[\alpha]_{5461}^{20}$	Dipole moment of the solvent $\times 10^{18}$ e.s.u.
Benzene	0.08	+0.21°	+66°	0
Chloroform	0.392	+0.81	+52	1.18
Ethyl Alcohol	0.372	0	0	1.63
Methyl Alcohol	0.378	0	0	1.64
Acetone	0.40	-0.39	-25	2.76
Nitrobenzene*	0.324	-0.49	-76	3.98

* In this case a 2 decimeter tube was used.

For the purpose of comparison, the dipole moments of the solvents have been included in the table. It will be seen that the specific rotation is thus positive in the case of a non-polar solvent and becomes increasingly negative as the dipole moment of the solvent is increased. The number of solvents used was limited by the fact that the compound under examination was insufficiently soluble in the majority of organic solvents.

The rotation at different wave-lengths was tested in acetone solution at 20°. Acetone was chosen as the solvent since the solubility in benzene is very small, thus decreasing the reading. Among other solvents chloroform is one with which it is more difficult to obtain reliable results, and if nitrobenzene is employed the solute is not readily recovered. In the following

a 2 decimeter tube was used.

Wave-length λ	Concentration c	α	$[\alpha]$
(Red) 6560 Å	1.184	-0.43°	-18°
(Green) 5461	1.184	-0.59	-25
(Blue) 4710 *	1.184	(-0.68)	(-29)

* This result was very inaccurate due to the extreme difficulty of reading the polarimeter when using blue light. The results are, however, sufficient to show that the dispersion is normal, i.e. the rotatory power increasing in magnitude as the wave-length decreases.

Purification of Solvents.

Pure chloroform, pure absolute alcohol, B.D.H. acetone, from the bisulphite compound, B.D.H. extra pure benzene (for molecular weight determinations) were used without further purification.

Methyl alcohol was refluxed for 8 hours over magnesium turnings and distilled.

Nitrobenzene was dried and distilled under reduced pressure.

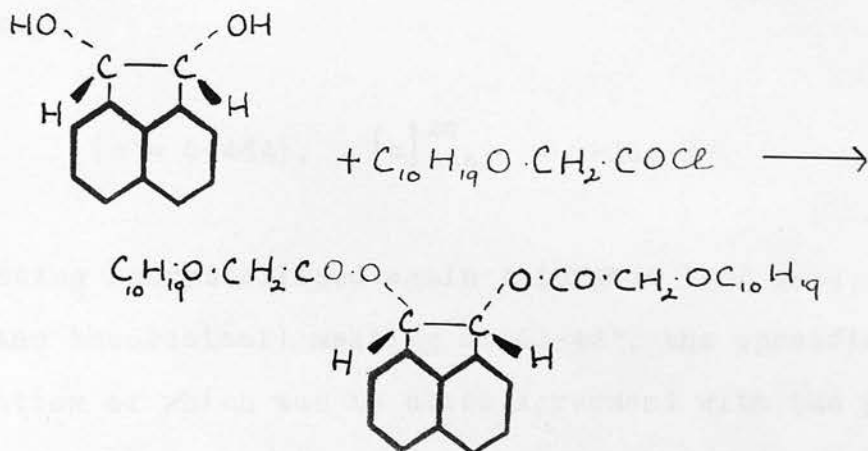
Attempt to prepare Acetyl Derivative of resolved
trans-Acenaphthylene Glycol.

0.04 gm. Resolved trans-acenaphthylene glycol.

5 ccs. acetic anhydride.

This mixture was boiled under reflux for 3/4 hour then poured into water. An oil was formed. The acetic acid thus formed was then neutralised with sodium hydroxide and the ester extracted with ether. On evaporation of the ether a very small quantity of a crystalline compound was deposited on the crystallising dish. The substance was, however, slightly sticky so that it could not be introduced into a melting point tube, and there was an insufficient quantity for recrystallisation or analysis. As no more resolved product was available this preparation was left unfinished.

Preparation of the di-*l*-Menthoxy Acetate of
cis-Acenaphthylene Glycol.



This preparation was carried out in the same way as the esterification of the corresponding trans-glycol.

4 gms. cis-Acenaphthylene glycol
 12 gms. *l*-menthoxy acetyl chloride
 30 ccs. pyridine.

The glycol was dissolved in pyridine and the acid chloride added gradually. After heating under reflux on an oil bath at 100° for $1\frac{1}{2}$ hours, the resulting brownish solution was poured into dilute hydrochloric acid, extracted with ether and the extract washed with sodium hydroxide solution followed by water. The ethereal solution was then dried over calcium chloride and the ether removed by evaporation. After some days the sticky oil had solidified to a microcrystalline mass (10.9 gms.). This was recrystallised three times from petrol ether (b.p. $40-60^\circ$). On being recrystallised for a fourth time,

1.42 gms. melting at 40-42° was obtained. The rotatory power was tested and it was found that, in benzene solution,

$$(c = 0.464), \quad [\alpha]_{5461}^{20} = -113.1^{\circ}.$$

On being recrystallised again this gave 1.22 gms., (10% of the theoretical) melting at 40-42°, the specific rotation of which was in close agreement with the previous result,

$$(c = 0.418), \quad [\alpha]_{5461}^{20} = -114.8^{\circ}.$$

On further recrystallisation no change in melting point occurred, but the compound did not have the normal appearance of a pure organic compound and the crystals always formed in hard crusts. Several other solvents, such as aqueous alcohol, were tried with no greater success.

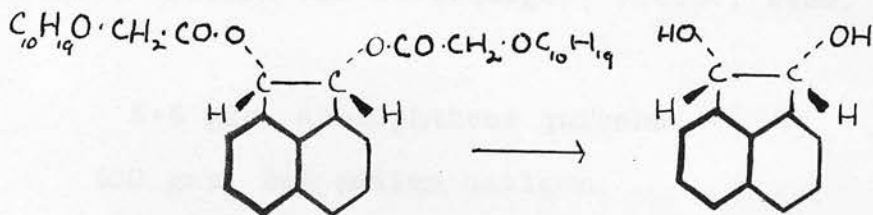
Analysis proved this compound to be the di-*l*-menthoxy acetate of acenaphthylene glycol.

Analysis:

Found, C: 74.8% , H: 8.9%.

Calculated for $C_{36}H_{50}O_6$, C: 74.7% , H: 8.7%.

Hydrolysis of the di-*l*-Menthoxo Acetate of
cis-Acenaphthylene Glycol.



0.63 gm. di-*l*-Menthoxo acetate of cis-acenaphthylene glycol

0.70 gm. potassium hydroxide

15 ccs. alcohol.

This mixture was heated on a steam bath under reflux for 4 hours, and some of the alcohol evaporated off. On addition of water, 0.18 gm. (90% of the theoretical) of a glycol was deposited in the form of white needles, melting at 201-203°. This, when recrystallised, yielded 0.15 gm. (m.p. 205-207°). The rotatory power of this compound was tested in acetone and methyl alcohol and found, in each case, to be zero. Two solvents having different dipole moments were used since, in the case of the resolved trans-acenaphthylene glycol, the specific rotation varied with the dipole moment of the solvent used and was, in certain solvents, zero or too small to be determined. The mixed melting point of this substance with cis-acenaphthylene glycol confirmed the fact that the original glycol had been regenerated.

Reduction of Acenaphthene Quinone with Sodium Amalgam.

Reference: Blount and Weissberger, J.C.S., 1936, 336.

5.5 gms. Acenaphthene quinone.

300 gms. 2½% sodium amalgam.

200 ccs. absolute alcohol.

The quinone and sodium amalgam were placed in a round-bottomed flask, fitted with an efficient mercury-sealed stirrer, a tap funnel, and a liquid seal for escape of gas. Nitrogen, from a cylinder, was passed into the flask continuously. The alcohol was added through the tap funnel, after the oxygen had been swept out of the apparatus by nitrogen, and in the first experiment, the nitrogen was not led actually into the liquid. The flask was placed on a water bath at 50° and the mixture stirred for 24 hours. The solution became dark blue and much blue solid separated. Finally, the blue colour faded and the solution remained greenish in colour, only a little solid being left undissolved.

Glacial acetic acid, 20 ccs., and water, 50 ccs., were then added through the tap funnel, causing the solution to become yellow and to effervesce, due to the decomposition of the remaining amalgam.

The mercury was separated and the solution was then filtered through charcoal and water added. A yellow ochre precipitate, which looked like the quinone, was

deposited and filtered off. The melting point, however, was not sharply defined. If heated slowly in a melting point tube the substance darkened at about 160° and appeared to soften about 190° , but did not melt completely whereas, if the tube were placed directly into the heated oil at a temperature of 150° the substance appeared to melt, with decomposition, immediately. The quinone melts at 260° . On evaporation of the mother liquors white needles were obtained which appeared to be sodium ethoxide and there was no trace of any glycol.

It was thought that possibly the reaction might have been retarded due to the presence of a little oxygen. The method of preparation was accordingly modified.

This mixture of quinone, amalgam and alcohol, as given above, was placed in the flask as before, but, in this instance, nitrogen from the cylinder was first passed through three wash bottles of freshly-prepared pyrogallol solution to remove any oxygen, and was bubbled continuously into the liquid. The mixture was stirred at 50° for 24 hours, as in the previous experiment. The solution became dark blue and, by the end of 24 hours, most of the blue solid which had formed was dissolved and the solution was lighter in colour. Glacial acetic acid, 20 ccs., and water, 50 ccs., were then added through the tap funnel. The solution again became yellow in colour and effervescence occurred. The mercury was separ-

ated and any insoluble material removed by filtration. Some water was added, and the resulting whitish precipitate was filtered off. This precipitate contained sodium, as was shown by a flame test, and was therefore boiled with a little water, allowed to cool, filtered and washed with hot water. The residue appeared to melt, with darkening, at 195-205°, but a metallic residue remained when a sample was burned on a platinum foil. Recrystallisation from alcohol was attempted, but the substance did not appear to be very soluble and the precipitate, on cooling, did not show any definite crystal form. Various solvents were tried but none seemed very suitable. Finally the solid was dissolved in ethyl acetate and the insoluble residue, which contained sodium, filtered off. On addition of petrol ether (b.p. 40-60°), a yellow precipitate was obtained, m.p. 230-240°. A mixed melting point with the original acenaphthene quinone confirmed that this yellow substance was the unchanged quinone.

The original aqueous alcohol solution, from which this material had been separated, was evaporated, and 2 gms. (38% of the theoretical) of crude material, m.p. 202-203°, was obtained. On recrystallisation from aqueous alcohol, however, instead of the expected white needles of cis-acenaphthylene glycol white plate-like crystals were obtained and a mixed melting point with cis-acenaphthylene^{glycol} proved that a different substance had been prepared. The melting point, by repeated recryst-

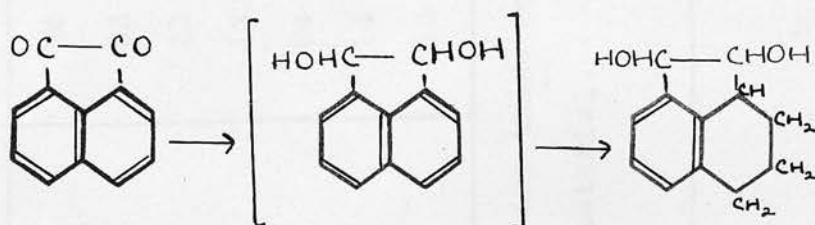
tallisation, was raised to 208.5-209°. Analysis proved this compound to be a tetrahydro-acenaphthylene glycol; confirmed later by the preparation of the diacetate (see p. 72).

Analysis:

Found, C: 75.5%, H: 7.3%

Calculated for $C_{12}H_{14}O_2$, C: 75.8%, H: 7.4%.

The fact that some unchanged acenaphthene quinone was isolated would appear to indicate that the reduction led first to the formation of acenaphthylene glycol which then underwent rapid reduction to the tetrahydro glycol. Blount and Weissberger, while claiming to have prepared cis-acenaphthylene glycol, quote neither a melting point of the purified product nor any analysis figures.

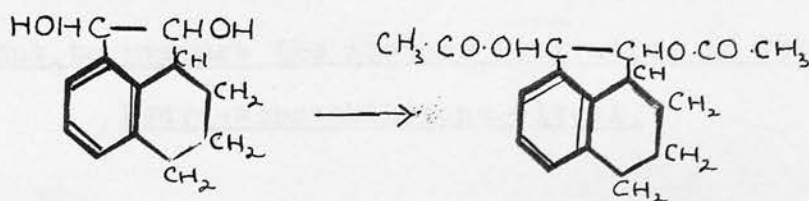


The conditions of the experiment were varied and the best yield (32% of the theoretical) was obtained when the mixture was stirred for 24 hours at 65-70°, using a slightly larger proportion of sodium amalgam. The table (on p. 71), however, does not give a very good indication of the manner in which the yield changes with temperature, or duration of the reduction owing to the

variable and unknown loss of glycol which may occur when unchanged quinone is thrown out with water. Had it been possible to work with larger quantities, this loss could probably have been brought down to a standard and minimum quantity.

When the tetrahydro glycol dissolved in warm chloroform was treated with a solution of bromine in the same solvent no decolourisation occurred. It may therefore be concluded that all four hydrogen atoms have entered the same ring in the naphthalene nucleus. The compound must therefore be a 1.2.3.4-tetrahydro-acenaphthylene glycol.

Preparation of the Acetyl Derivative of Tetrahydro-acenaphthylene Glycol.



0.3 gms. Tetrahydro-acenaphthylene glycol.

15 ccs. acetic anhydride.

The above mixture was heated under reflux. The glycol dissolved gradually on heating and, after half an hour, the solution was poured into a large quantity of water. An almost white solid was precipitated, fil-

tered off and dried. A yield of 0.43 gm., (quantitative) melting at 134.5-136° was obtained, and this on recrystallisation from aqueous alcohol gave 0.37 gm. of colourless plates, m.p. 139-140°. Further recrystallisation did not raise the melting point.

Analysis:

Found , C: 70.1%, H: 6.5%

Calculated for diacetate of
tetrahydro-acenaphthylene
glycol, $C_{16}H_{18}O_4$,

C: 70.1%. H: 6.6%.

Rast molecular weight determination.

Found, 249.

Calculated for $C_{16}H_{18}O_4$, 274.

Attempt to prepare the Acetone Derivative of Tetrahydro-acenaphthylene Glycol.

0.3 gm. Tetrahydro-acenaphthylene glycol.

5 ccs. acetone, dried over anhydrous sodium
sulphate and containing 1% HCl.

a little anhydrous sodium sulphate.

This mixture was allowed to stand at 15° for 24 hours. The glycol did not appear to be completely dissolved. More dried acetone was added and the mixture

heated gently to dissolve all the glycol. The hydrochloric acid was removed by passing dry ammonia into the solution, thus precipitating ammonium chloride, which was then filtered off. The acetone was removed by evaporation and a residue of 0.29 gm. of white, plate-like crystals (m.p. 206-207°) obtained. A mixed melting point with the original glycol established this substance as the starting material.

To confirm this experiment another method was used (Pascu, Ber., 1924, 57, 849). Acetone was dried over anhydrous sodium sulphate and to 90 ccs. of the dry liquid was added 1 cc. of concentrated sulphuric acid: 5 ccs. of this mixture and 0.3 gm. tetrahydro-acenaphthylene glycol were allowed to stand for 24 hours at 15° and then treated in exactly the same way as in the previous experiment. Only unchanged glycol was recovered.

Preparation of the di-*l*-Menthoxo Acetate of Tetrahydro-acenaphthylene Glycol.

8 gms. Tetrahydro-acenaphthylene glycol.

70 ccs. pyridine.

25 gms. *l*-menthoxy acetyl chloride.

The above mixture was heated under reflux for 1½ hours at 100° on an oil bath. The solution was poured

into dilute hydrochloric acid and extracted with ether in exactly the same manner as the corresponding ester of trans-acenaphthylene glycol (see p. 58).

22.9 gms. of crude micro-crystalline compound were obtained. This was recrystallised from petrol ether (b.p. 40-60°) the product of the first few recrystallisations being very sticky. After being recrystallised five times 4.7 gms. of a whitish substance melting at 66-70° was obtained. This substance did not have the appearance of a pure compound and the crystal structure was not very definite. The rotatory power was tested in benzene solution.

$$(c = 0.412), [\alpha]_{5461}^{20} = -91^{\circ}.$$

On continued recrystallisation the melting point was raised to 71-72°, but not further. The specific rotation of the product remained constant at -94°.

Yield, 3.2 gms. (23% of the theoretical).

$$(c = 0.484), [\alpha]_{5461}^{20} = -94^{\circ}.$$

On standing for about two weeks, the oily material which was left when the petrol ether evaporated off from the original mother liquors from this experiment, was found to contain a large proportion of clean looking crystals. The oil was filtered off as far as possible and the crystalline mass spread out on a porous plate

for a few days. On recrystallisation from petrol ether, 1.4 gms. of a white substance (m.p. 70-72°) was obtained which still did not crystallise very satisfactorily. Rotatory power in benzene solution,

$$(c = 0.52), [\alpha]_{5461}^{20} = -96^{\circ}.$$

The fact that the melting point and specific rotation of this material, obtained from the first mother liquors of the ester, are in agreement with the corresponding data for the main product resulting from repeated recrystallisation, suggest that the original tetrahydro-acenaphthylene glycol has not undergone any optical resolution by being converted into the *l*-menthoxy acetate and fractionated.

It was found later that the ester, on recrystallisation from aqueous alcohol, could be obtained in good crystalline form as colourless needles, although the melting point (71-72°) was unchanged. A sample of this was used for analysis.

Analysis:

Found,	C: 73.9%, H: 9.1%.
Calculated for $C_{36}H_{54}O_6$,	C: 74.2%, H: 9.3%.

Hydrolysis of the di-*l*-Menthoxo Acetate of Tetra-
hydro-acenaphthylene Glycol.

0.8 gm. di-*l*-Menthoxo acetate of tetrahydro-
acenaphthylene glycol.

15 ccs. 10% sodium hydroxide solution.

10 ccs. acetone.

This mixture was heated on the steam bath for $2\frac{1}{2}$ hours. The solid melted and formed an oil, which gradually turned slightly brownish in colour and in which a few crystals appeared. The mixture was extracted twice with ether and the ether evaporated off. Some crystals appeared in the crystallising dish but there appeared to be a certain amount of oil present. Yield, 0.34 gm. On being recrystallised from aqueous alcohol, 0.24 gm. of white needles, melting at $71-72^{\circ}$, was obtained. The specific rotation, which was tested in benzene solution, and the mixed melting point with the unhydrolysed ester, proved this to be the unchanged starting material.

$$(c = 0.518) \quad [\alpha]_{5461}^{20} = -94^{\circ}.$$

On further extraction with ether 0.13 gm. (i.e. equivalent to 0.39 gm. of the ester) of a glycol, melting at $204-206^{\circ}$, was obtained.

It was decided to use more vigorous conditions for

the hydrolysis.

1 gm. di-*l*-Menthoxo acetate of tetrahydro-acenaphthylene glycol.

1 gm. potassium hydroxide.

25 ccs. alcohol.

The above mixture was heated under reflux for $4\frac{1}{2}$ hours on a steam bath, then some of the alcohol evaporated off. On addition of water, a white crystalline precipitate was deposited. This was filtered off and dried giving 0.3 gm. of white plates (94% of the theoretical), melting at 197-199°. On recrystallisation from alcohol, this yielded 0.22 gm., m.p. 208-209°. The rotatory power was tested in acetone and methyl alcohol and found in each case to be zero. Here, as in the case of the ester of cis-acenaphthylene glycol, two solvents were used, lest the compound should have a rotation which, in varying with the dipole moment of the solvent, should in one case be zero. The zero result in two solvents, however, and the mixed melting point with the original tetrahydro-acenaphthylene glycol, proved that no resolution had occurred.

Attempted Reduction of cis-Acenaphthylene Glycol
by means of Zinc and Potassium Hydroxide.

0.5 gm. cis-acenaphthylene glycol.

1 gm. zinc dust.

0.5 gm. potassium hydroxide

5 ccs. water.

5 ccs. alcohol.

The above mixture was boiled for about 20 minutes. More alcohol was added to keep all the organic material in solution, and the zinc was then filtered off. On cooling, 0.42 gm. of white needles (m.p. 207-208°) was obtained. A mixed melting point proved this to be unchanged cis-acenaphthylene glycol. On evaporation of the mother liquors a further quantity of the same substance was obtained.

Attempted reduction of cis-Acenaphthylene Glycol
by means of Sodium and Amyl Alcohol.

1 gm. cis-Acenaphthylene glycol.

40 ccs. amyl alcohol.

1.5 gms. sodium.

The glycol was dissolved in the amyl alcohol and heated to boiling point, the sodium being then added in small pieces. Continued heating was necessary to dis-

solve the last pieces. The solution became deep blue in colour, fading to a greenish blue. The amyl alcohol was removed by steam distillation, and in the course of this treatment the solution became yellow in colour and a precipitate was formed. By the time all the amyl alcohol was removed, however, the original precipitate had been converted into a yellowish brown oil. On shaking up with ether the oil dissolved forming a yellow ethereal layer with quite a strong purple fluorescence. The ether layer was dried over calcium chloride and the ether removed by evaporation. A slight residue of yellowish oil containing a very little solid was obtained, but was insufficient for further purification. The amyl alcohol and water, collected from the steam distillation, on evaporation to dryness gave no appreciable residue. The aqueous layer from the ether extraction, on evaporation gave a black tar.

This experiment was repeated, but no pure product could be isolated.

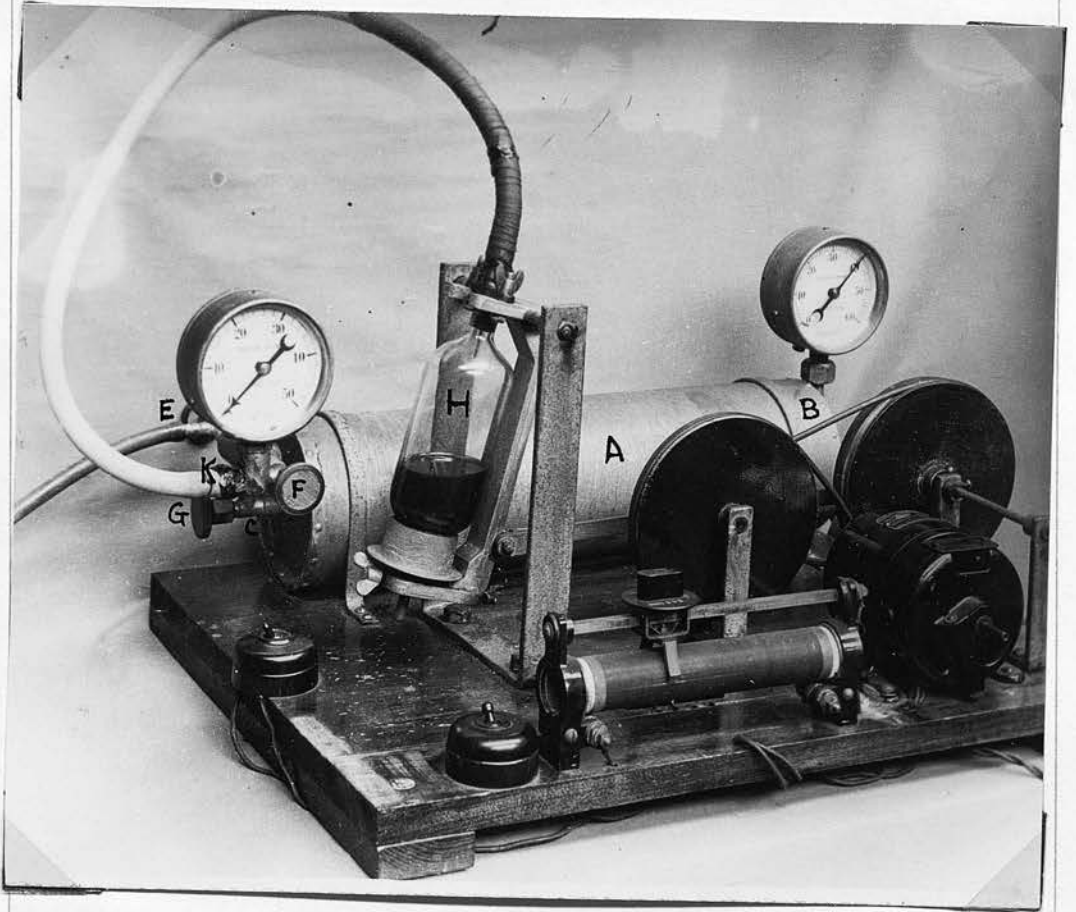


Fig. 2.

Catalytic Hydrogenation of Acenaphthylene Glycols.

The apparatus (fig. 2) employed was similar to that used by Buck and Jenkins (J.A.C.S., 1928, 51, 2163).

A cylindrical copper tank A with openings B and C at either end is used as a container for the hydrogen gas. In B is welded a tube holding a Bourdon pressure gauge and a needle valve, through which the container is charged from a cylinder of hydrogen. In C is welded another tube controlled by a needle valve G. Into this tube is welded a third tube K with needle valves E and F at either end. Valve E is used for evacuating the apparatus, and valve F connects to the reaction bottle H, the arrangement being such that the tank A can be shut off from either outlet, and direct connection made between the evacuating pump and the bottle, thus cutting the tank out of the circuit. Between the valve F and the bottle H is a second Bourdon gauge which indicates the pressure inside the bottle.

The connection between the tank and the bottle is made by means of heavily taped rubber tubing, which is connected to a capillary glass tube inserted through the rubber stopper of the bottle.

The reaction bottle, of 300 ccs. capacity, is of thick pyrex glass, capable of withstanding a pressure of 200 lb./sq.in. It is held secure in a rocking frame, which is rocked with variable speed by means of a stiff

connecting rod and fly wheel, driven by a motor with rheostat. In order to hold the stopper in the bottle when the latter is filled with hydrogen under pressure, a metal strap fixed between the stopper and the rubber tubing is firmly clamped on top of the rocking frame.

The bottle is heated, if necessary, by means of an external electrically heated coil of wire wound on a cylindrical asbestos shell. A variable resistance in the circuit is used to regulate the temperature.

The whole apparatus is rigidly fixed to a heavy wooden base.

Use of the Apparatus.

In using the apparatus it is essential to guard against leaks.

The apparatus is first tested for a leak. The reduction bottle is attached to the apparatus, exactly as for a hydrogenation experiment, and is filled with hydrogen to a pressure of about two atmospheres. As soon as equilibrium is reached the temperature and pressure are recorded and the bottle allowed to shake for six hours. If the drop in pressure is less than 0.5 lbs. the apparatus is considered to be satisfactory.

The tank A is then filled with hydrogen to a pressure of 4-5 atmospheres. The solution, in a suitable solvent, of the substance to be hydrogenated is introduced into the bottle and the catalyst added.

The bottle is attached to the apparatus and evacuated, the valves E and F being open and G closed. Evacuation is continued until the pressure is constant, or, in the case of low boiling solvents, until the solvent just begins to boil. The valve E is then closed and hydrogen admitted to the bottle by opening the valve G. The valve F is closed, and the pressure of the hydrogen in the bottle is read on the gauge. Shaking is commenced, and continued until the desired amount of hydrogen has been absorbed. The hydrogen remaining in the bottle is then removed and air admitted.

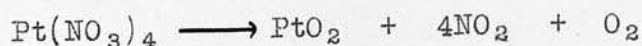
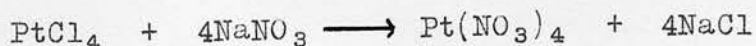
The catalyst is recovered by filtering the solution through a hardened filter paper, and the reduction product isolated by evaporation of the solvent or addition of water.

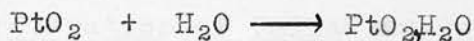
Calibration of Apparatus.

A preliminary calibration of the apparatus was carried out for the absorption of one and two proportions of hydrogen, using 0.01 mole of pure benzoin and benzil respectively as standards. Complete hydrogenation to hydrobenzoin corresponded in the first case to a fall of 16 lbs./sq.in. in pressure, and in the second case to 32 lbs./sq.in.

Preparation of the Platinum Catalyst.

Reference: Adams, Vorhees and Shriner (Org. Syn., 1928, 8, 92)





18 gm. sodium nitrate, A.R.

2 gm. alkali-free platinum chloride

dissolved in 6 ccs. water.

The sodium nitrate was added to the platinum chloride solution in a porcelain casserole, and the mixture carefully evaporated to dryness. The temperature was raised gradually, and the full force of the Bunsen burner directed on the casserole for 30 minutes. The mass was allowed to cool and treated with 50 ccs. of water. The brown oxide (1.1 gm.) was washed by decantation, filtered through hardened filter paper on a Gooch crucible, washed until free from nitrates and dried in a vacuum desiccator.

"Exhausted" catalyst was reactivated by dissolving in aqua regia, filtering, evaporating to dryness three times with hydrochloric acid and then with a little water, and finally fusing in the ordinary way with sodium nitrate.

Preparation of Palladium Catalyst.

20 gms. of freshly prepared barium sulphate was added to 450 ccs. of hot water. To this was added 1.7 gms. of palladium chloride in 50 gms. of water and also 1 gm. formalin (40%). The mixture was made slightly alkaline with sodium hydroxide and heated for a time to boiling. When the supernatant liquid was clear and colourless, the grey substance was filtered off and washed with hot water until the washings were neutral to litmus. The catalyst was then dried in vacuo over potassium hydroxide.

Ordinary commercial hydrogen was found to be quite efficient for the reductions.

Hydrogenation of cis-Acenaphthylene Glycol using
Platinum Catalyst.

Hydrogenation of cis-acenaphthylene glycol was attempted under various conditions. The first solvent used was glacial acetic acid, but after about a third of the desired amount (2 moles) of hydrogen had been absorbed, further absorption became very slow and it was decided to repeat the experiment with heating.

The experiment was accordingly repeated, with addition of 5 ccs. of concentrated hydrochloric acid and a few drops of ferric chloride as an accelerator, the mixture in this instance being heated to about 50°. The colour of the solution changed to yellow, orange and finally brownish and again absorption seemed to be arrested before the required amount of hydrogen had been taken up. In this case the copper of the valves of the apparatus had been attacked by the acid solvent and possibly the catalyst had thus become poisoned. On addition of water to the yellow solution, obtained by filtering off the catalyst, an orange coloured oil was precipitated. This may have been due to acetylation occurring.

It was then decided to use alcohol as a solvent and to carry out the reduction with heating.

1.86 gms. (0.01 mole) cis-acenaphthylene glycol
50 ccs. alcohol
0.1 gm. platinum catalyst
a few drops of concentrated hydrochloric acid.

The above mixture was introduced into the reaction vessel, the air removed by suction, and hydrogen admitted. After the pressure in the bottle had been read on the Bourdon gauge, shaking and heating were started. As the mixture heated up the glycol all passed into solution. When the required amount of hydrogen (2 moles) had been absorbed, the experiment was stopped. On cooling no crystals appeared, the reduction product remaining entirely in solution. The catalyst was removed by filtration through a hardened filter paper and, as addition of water to a test portion appeared to cause the separation of a liquid product, the solution was evaporated slowly, to small volume. Finally 1.78 gms. of a hard solid mass was obtained. This appeared to be a mixture from the behaviour in a melting point tube, when some softening occurred below 100° , while complete fusion occurred at about $180-190^{\circ}$. On boiling with 50 ccs. of water some oil (A) was obtained and removed by filtration of the hot mixture.

Evaporation of the filtrate gave 0.5 gm. of white crystals (m.p. $92-94^{\circ}$), which after recrystallisation from ligroin formed white needles, m.p. $92.5-93.5^{\circ}$.

Yield, 0.25 gm. Further recrystallisation did not raise the melting point beyond this temperature.

Analysis proved that a tetrahydro-acenaphthylene glycol had been obtained, confirmed later by preparation of the diacetate. (see p. 90)

Analysis.

Found, C: 75.4%, H: 7.0%.

Calculated for $C_{12}H_{14}O_2$, C: 75.7%, H: 7.3%.

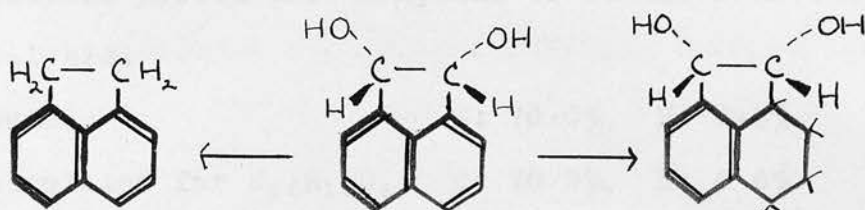
A solution of this compound, dissolved in warm chloroform, did not decolourise bromine. It may therefore be concluded that all four hydrogen atoms have entered the same ring in the naphthalene nucleus and that the compound is therefore 1.2.3.4-tetrahydro cis-acenaphthylene glycol.

After standing for a few days the oil A was found to contain rectangular, plate-like crystals. The mixture was transferred to a porous plate and the dry crystals found to have a melting point of about 89°. On recrystallisation from petrol ether (b.p. 40-60°) stout needles were obtained the melting point of which was 92°, but there was insufficient substance left for further recrystallisation or for analysis. This compound gave a mixed melting point with the above cis-tetrahydro-acenaphthylene glycol_{of} about 80°.

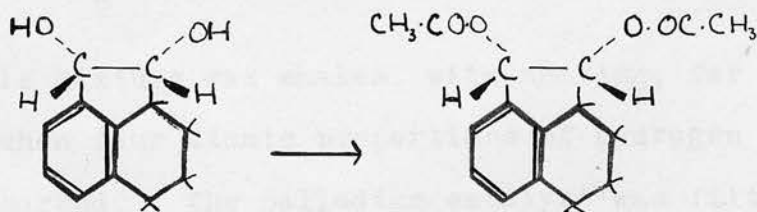
An attempt to repeat this experiment in order to obtain more of the unidentified product was unsuccessful, possibly due to some unknown impurity inhibiting

the reactivity of the catalyst. Since palladium catalyst is less easily poisoned it was used in the next experiment.

Actually it was found later that the unidentified compound was acenaphthene (m.p. 95°) so that the reactions occurring are probably to be represented by the following scheme:



Preparation of the Acetyl Derivative of the Tetrahydro-acenaphthylene Glycol obtained by Hydrogenation of cis-Acenaphthylene Glycol.



0.18 gm. of the glycol (m.p. 92.5-93.5)

1 cc. acetic anhydride.

The above mixture was refluxed for $\frac{3}{4}$ hour. The glycol dissolved on heating, and on addition of water a

white solid was precipitated and filtered off. A yield of 0.23 gm. (quantitative) of a substance melting at 108-110° was obtained, which on recrystallisation from petrol ether (b.p. 40-60°), gave 0.13 gm. of white needles, m.p. 120-121°. Further recrystallisation raised the melting point to 121-121.5°.

Analysis proved this compound to be the diacetate.

Analysis.

Found, C: 70.0%, H: 6.3%.

Calculated for $C_{16}H_{18}O_4$, C: 70.0%, H: 6.6%.

Hydrogenation of cis-Acenaphthylene Glycol using
Palladium Catalyst.

1.9 gms. cis-Acenaphthylene glycol

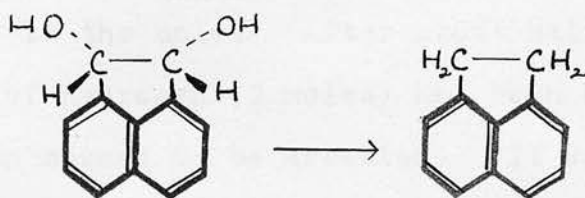
50 ccs. alcohol

0.5 gm. palladium catalyst.

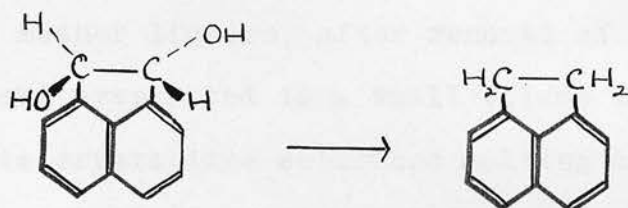
This mixture was shaken, with heating, for 12 hours, when four atomic proportions of hydrogen had been absorbed. The palladium catalyst was filtered off from the warm solution and white needles, thicker than those of the original glycol, were obtained on cooling. These crystals gave a melting point of 92-93°. On addition of water a further quantity of the same substance (confirmed by mixed melting point) was deposited. The total yield was 1.5 gm. On recryst-

tallisation from alcohol the melting point was raised to 93-94°.

This compound, when mixed with the tetrahydro-acenaphthylene glycol obtained in the previous experiment, melted at about 77°, but no depression of melting point occurred when it was mixed with the unidentified compound (A) isolated in the same experiment. It was at first assumed that a reduced glycol had been obtained, but experiment showed that the compound could not be acetylated. This suggested that the 1:8-bridge had undergone complete reduction to the hydrocarbon stage, a conclusion which was confirmed by carrying out a mixed melting point of the above compound with acenaphthene, m.p. 95°, when no depression was observed.



Hydrogenation of trans-Acenaphthylene Glycol using
Palladium Catalyst.



1.86 gms. trans-Acenaphthylene glycol
 50 ccs. alcohol
 0.5 gms. palladium catalyst.

The above mixture was treated in the hydrogenation apparatus, with heating. In this case the glycol all dissolved in the cold. After about half the desired quantity of hydrogen (2 moles) had been absorbed further absorption seemed to be arrested. It was thought the catalyst might be poisoned and the experiment was accordingly stopped and the catalyst filtered off and fresh catalyst added. On further treatment for several hours, however, no further absorption took place and the experiment was again stopped and a few drops of concentrated hydrochloric acid and a few drops of ferric chloride solution were added, but no further hydrogenation could be effected. The catalyst was therefore removed by filtration and, on addition of water to the filtrate, a

white precipitate was obtained. This precipitate was filtered off and found to melt at 93-94° and a mixed melting point proved that acenaphthene had been isolated. Yield, 0.6 gm.

The mother liquors, after removal of the acenaphthene, were evaporated to a small volume and 0.67 gm. of a white crystalline substance melting at 157-158° obtained. A mixed melting point proved this to be unchanged trans-acenaphthylene glycol.

Hydrogenation of trans-Acenaphthylene Glycol using
Platinum Catalyst.

1.86 gms. (0.01 mole) trans-Acenaphthylene glycol
50 ccs alcohol

0.1 gm. platinum catalyst

a few drops of concentrated hydrochloric acid

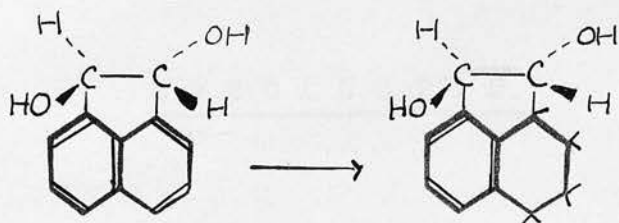
a few drops of ferric chloride.

The above mixture was shaken with heating (50°) under hydrogen for about 7 hours, when the desired amount of gas was absorbed. The platinum catalyst was removed by filtration and, on addition of water, a copious white precipitate obtained. This substance, which was in the form of crystalline plates, melted at 207-208° and a mixed melting point with the tetrahydro-acenaphthylene glycol obtained by reduction of acenaphthene quinone with sodium amalgam proved that the same com-

pound had been obtained.

On evaporation of the mother liquors a further quantity of the same material was isolated. The total yield was 1.4 gms. (75% of the theoretical)

This compound has already been proved to be a 1.2.3.4-tetrahydro-acenaphthylene glycol (see p. 70). Its preparation from trans-acenaphthylene glycol thus completely establishes its identity as 1.2.3.4-tetrahydro trans-acenaphthylene glycol.



CONCLUSION.

The preparation of acenaphthylene from acenaphthene has been carried out under varying conditions, and a maximum yield of about 50% has been obtained. From acenaphthylene the acenaphthylene glycols have been prepared by way of the dibromides. In this case various modifications have been introduced into the methods described in the literature. The direct oxidation of acenaphthylene to the glycols was attempted but found to be unsuccessful.

Several methods of purification of the lower melting (trans-) modification of the glycol have been used, the most satisfactory being the removal of the higher melting (cis-) glycol in the form of its acetone compound.

That the higher melting form of acenaphthylene glycol is of cis- and the lower melting form of trans-configuration, has been further established by the optical resolution of the lower melting glycol. This was effected by converting it into the di-*l*-menthoxy acetates, followed by fractionation. Hydrolysis of the resulting highly laevorotatory ester yielded an optically active trans-acenaphthylene glycol. The specific rotation of this compound was found to vary with the solvent used, being positive in solvents of low dipole moment, and negative in solvents of high dipole moment, while for solvents of intermediate polarities (e.g. ethyl and methyl

alcohol), the specific rotation was found to be zero, or too small to be determined.

The higher melting acenaphthylene glycol, on conversion to the di-*l*-menthoxy acetate, fractionation and hydrolysis of the pure ester obtained, was recovered unchanged, in agreement with its established *cis*-configuration.

An attempt to prepare acenaphthylene glycol by a method recently described by Blount and Weissberger, by reduction of acenaphthene quinone with sodium amalgam, led to the isolation of a 1.2.3.4-tetrahydro acenaphthylene glycol. The resolution of this compound was attempted, in a similar manner to *trans*-acenaphthylene glycol, but without success.

As four racemic 1.2.3.4-tetrahydro acenaphthylene glycols are possible, the hydrogenations of the *cis*- and *trans*-acenaphthylene glycols were carried out in order to determine, if possible, whether the compound obtained by the chemical reduction was of *cis*- or *trans*-configuration.

It was found that, using platinum oxide as a catalyst two 1.2.3.4-tetrahydro acenaphthylene glycols could be isolated. One of these, prepared from *trans*-acenaphthylene glycol, was identical with the compound obtained by chemical reduction of acenaphthene quinone, which must therefore be of *trans*-configuration. The other 1.2.3.4-tetrahydro acenaphthylene glycol prepared

from cis-acenaphthylene glycol was quite a different compound.

Using palladium deposited on barium sulphate as catalyst, however, both cis- and trans-acenaphthylene glycol, on hydrogenation, were converted into the hydrocarbon acenaphthene.

It thus appears that the catalysts have a specific effect, hydrogenation, using palladium as a catalyst, tending to take place more readily at the hydroxyl groups, whereas, when platinum is used the reduction occurs more readily within the naphthalene nucleus.

In conclusion the author wishes to express her appreciation of Dr. H. G. Rule's helpful advice and unfailing interest throughout the course of the work. Thanks are also due to the Edinburgh Angus Club for a Strathmore-Cobb Scholarship, during the tenure of which this research was carried out.